CA/DOH/AIHL/SP 23

EVALUATION AND DEVELOPMENT OF PROCEDURES FOR DETERMINATION OF SULFURIC ACID, TOTAL PARTICLE-PHASE ACIDITY AND NITRIC ACID IN AMBIENT AIR-PHASE II

(Contract No. ARB A8-111-31)

Final Report

October 1980

Prepared by

B. R. Appel, Y. Tokiwa, E. M. Hoffer
E. L. Kothny, M. Haik and J. J. Wesolowski

Air and Industrial Hygiene Laboratory
Laboratory Services Branch
California Department of Health Services
2151 Berkeley Way
Berkeley, California 94704

Prepared for: California Air Resources Board
Research Section
P.O. Box 2815
Sacramento, California 95812

The statements and conclusions in this report are those of the Contractor and not necessarily those of the State Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

ABSTRACT

Methods for measurement of sulfuric acid, strong acids and nitrate in atmospheric particulate matter, and for gaseous nitric acid were evaluated. Selective extraction with benzaldehyde and titrimetry for strong acids were compared in atmospheric trials. Gaseous nitric acid was determined by 1) measuring the nitrate collected on nylon or NaCl-impregnated cellulose filters after removal of particulate matter with Teflon prefilters, and 2) the difference between total inorganic nitrate (TIN) and particulate nitrate (PN). TIN was measured by the sum of the nitrate collected with a Teflon prefilter and nylon or NaCl-impregnated after-filter. PN was measured by the nitrate able to penetrate a diffusion denuder coated to remove acidic gases including HNO_3. Losses of nitrate from Teflon prefilters were determined by comparing the nitrate retained by these filters to the nitrate penetrating the acid gas denuder. TIN was compared with the nitrate collected on glass fiber filters to assess the origin of the artifact particulate nitrate on the latter. A modified chemiluminescent NO_x monitor converted to measure nitric acid continuously, was compared to the filter techniques.

Levels of H_2SO_4 up to 11 $\mu g/m^3$ were observed in California's South Coast Air Basin (SCAB) using selective extraction with benzaldehyde. Strong particulate acid measurements by titrimetry generally supported the H_2SO_4 determinations. However, HNO_3 appeared to contribute to the particulate acidity together with the H_2SO_4. Gaseous nitric acid measurements in the SCAB using nylon or NaCl-impregnated after-filters were substantially higher than those by the difference technique. This correlated with losses of nitrate from the Teflon prefilters, which exceeded 50% at high ambient temperature and low relative humidity. Heating the filter samplers was shown to increase sampling errors. Atmospheric nitrate results obtained in short-term, low volume sampling with Gelman A glass fiber filters approximated those with the TIN samplers. Accordingly, these glass fiber filters retained essentially all the gaseous nitric acid sampled.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF TABLES

LIST OF TABLES (continued)

ACKNOWLEDGEMENTS

FTIR measurements were made by E. C. Tuazon, Statewide Air Pollution Research Center, University of California (Riverside). The concept of measuring nitric acid as the difference between total inorganic nitrate and particulate nitrate determined using an acid gas denuder was devised by R. Shaw and co-workers, U. S. Environmental Protection Agency. The authors also express their appreciation to Professor G. Kok, Harvey Mudd College, and to the staff and management of the South Coast Air Quality Management District for providing facilities for atmospheric sampling. S. Twiss assisted with the data reduction and display.

J. Suder served as project officer for this program. His helpfulness throughout this work is sincerely appreciated.

This report was submitted in fulfillment of ARB Contract Number A8-111-31, Evaluation and Development of Procedures for Determination of Sulfuric Acid, Total Particle-Phase Acidity and Nitric Acid in Ambient Air--Phase II, by the Air and Industrial Hygiene Laboratory, Laboratory Services Branch, California Department of Health Services. Work was completed as of October 1, 1980.

I. INTRODUCTION

Phase I of this program investigated methods for the determination of sulfuric acid and strong acids in atmospheric particulates as well as nitric acid in ambient air. The procedures for particulate acids employed sampling with inert filters, processing the samples under conditions designed to preserve strong acids followed by analytical techniques appropriate for sulfuric acid (H_2SO_4) and strong acids. These techniques were evaluated and compared using laboratory-generated mixtures of $\leq$ 0.3 μm diameter H_2SO_4, $(NH_4)_2SO_4$, and NH_4HSO_4 aerosols on clean and atmospheric particulate-loaded filters. Based on filtration efficiencies and recovery studies with submicron sulfuric acid aerosol, acid-washed quartz fiber and one or two micron pore size Teflon membrane filters were employed. H_2SO_4 was determined by selective extraction with benzaldehyde followed by quantitation as sulfate by the AIHL microsulfate method. Strong acid was measured by microtitration with exclusion of carbon dioxide. Nitric acid was sampled by collection on nylon, and on sodium chloride-impregnated cellulose filters after removal of atmospheric particles with an inert prefilter. Following aqueous extraction, nitric acid was determined as nitrate by the automated copper-cadmium reduction, diazotization procedure.

The applicability and utility of these procedures were assessed by atmospheric sampling in Pittsburg, California. To stabilize strong acids on filters, > 3 μm particles, which can contain alkaline soil components, were excluded. In addition, with one sampler atmospheric ammonia was removed ahead of the filter by means of a diffusion denuder. Simultaneous gas phase ammonia measurements were made to assist in interpreting the particulate sample results.

The Phase I results showed that the presence of atmospheric particulate matter sharply reduced recoveries of laboratory-generated H_2SO_4 but recoveries of total strong acid usually remained $\geq$ 60%. Anhydrous benzaldehyde was found to extract NH_4HSO_4 to a substantial degree. Laboratory-generated nitric acid was collected with high efficiency by both nylon and NaCl-impregnated filters while nitrogen dioxide was not retained by these filters at 90% R.H. The ammonia denuder was shown to remove ammonia with > 99% efficiency.

The field sampling in Pittsburg, California showed good correlation between sulfuric acid and particulate strong acid measurements. As much as 0.6 $\mu g/m^3$ H_2SO_4 and 1.6 $\mu g/m^3$ acidity, expressed as H_2SO_4, was found.

However, based on recovery studies we believe these represent lower limit values. Excellent agreement was found between nitric acid measurement by nylon and NaCl on cellulose filter collection with concentrations up to 4 $\mu g/m^3$. Glass fiber filters were shown to collect, quantitatively, both particulate nitrate and gas phase nitric acid at the relatively low concentrations observed at Pittsburg.

The present phase of this study was designed to evaluate these sampling and analysis techniques at two locations in California's South Coast Air Basin (SCAB). One of the sites, Lennox, was expected to exhibit relatively high H_2SO_4 levels based on its proximity to sulfur oxide emission sources. The second site, Claremont, was in an area where high (> 50 $\mu g/m^3$) HNO_3 and particulate nitrate levels were expected. Improved procedures were employed to minimize losses of the particulate acids during sample storage and handling, and the analytical procedure was modified to reduce the limit of detection for H_2SO_4 with hi-vol filter samples. In addition to the nitrate and HNO_3 sampling techniques previously employed, the present study included a potential reference technique for particulate nitrate and HNO_3 measurement. This technique measures HNO_3 as the difference between total inorganic nitrate (gaseous plus particulate nitrate) and true particulate nitrate. HNO_3 and NH_3 results at Claremont were compared to those of the Statewide Air Pollution Research Center's Fourier transform, long path infra-red analysis method. The effect of atmospheric NH_3 on both nitrate and sulfate chemistry was also assessed.

Laboratory evaluations in the present phase included measurement of sampling errors for HNO_3 with filter techniques, and an evaluation of the potential reference technique for particulate nitrate and nitric acid. In addition, a continuous HNO_3 analyzer was constructed from a chemiluminescent NO_x monitor, and evaluated. Since the use of the NH_3 denuder in acid sulfate sampling may cause increased acid formation in particulate matter by loss of NH_3 from NH_4^+ salts, laboratory trials evaluated this possibility.

II. TECHNICAL SUMMARY AND CONCLUSIONS

A combined laboratory and field study has continued investigations of methods for monitoring atmospheric sulfuric acid, nitric acid and strong acids in atmospheric particulates. A potential reference technique for atmospheric HNO_3 and particulate nitrate was also investigated. Sulfuric acid was measured by selective extraction with benzaldehyde followed by quantitation as sulfate using the ATHL microchemical sulfate method. Nitric acid was measured by sampling with nylon or sodium chloride-impregnated cellulose filters following removal of particulate nitrates with a Teflon prefilter (1 or 2 μm pore size Zefluor, Ghia Corp.). Following aqueous extraction, nitric acid was measured as nitrate by the automated, copper-cadmium reduction diazotization procedure. Nitric acid was also measured continuously by a modified Monitor Labs chemiluminescent NO_x analyzer and by a newly proposed difference technique. The latter uses the sum of the nitrate retained by a Teflon prefilter and nylon or NaCl-impregnated after-filter to measure total inorganic nitrate (TIN). Particulate nitrate (PN) was measured with a Teflon prefilter plus after-filter following passage of the sample stream through a diffusion denuder coated with powdered MgO to remove acidic gases (e.g., HNO_3). TIN less PN provided a measure of the HNO_3 concentration. The TIN and PN samplers were evaluated as potential reference methods for HNO_3 and particulate nitrate. Particulate strong acid was measured by a microtitration procedure in which an amount of strong acid sufficient to produce pH = 4.0 in distilled water was added to each sample followed by potentiometric titration with base to this pH.

The laboratory phase of the H_2SO_4 and particulate acid method evaluation included an assessment of errors induced by use of an ammonia diffusion denuder. The latter was used in atmospheric sampling to minimize losses of the acid by neutralization with NH_3 and other gaseous bases following collection on a filter. In principle such a denuder could cause errors in measured H_2SO_4 and H^+ values by inducing loss of NH_3 from $(NH_4)_2SO_4$ and other ammonium salts. In addition any transfer to the filter of the NH_3-trapping reagent, phosphorous acid, would produce positive errors in the H^+ measurements. However, passage of clean air through the denuder followed by blank Teflon filters or filters loaded with $(NH_4)_2SO_4$ or $(NH_4)_2SO_4$-NH_4NO_3 mixtures caused no increase in acidity on the filters. Thus use of the ammonia denuder does not produce positive errors of this type.

Nitric acid sampling with filters was evaluated with and without filter heating (e.g., passing heated air through the sample for three minutes

following sampling) to desorb HNO_3 from sampler surfaces. The efficiency of NaCl-impregnated Whatman 41 cellulose filters (NaCl/W41) for HNO_3 collection remained about 97% under all conditions. However, with heated nylon filters the efficiency was low at high HNO_3 loadings (e.g., 30% for sampling of 2350 μg HNO_3, as NO_3^-). Unheated nylon filters provided 95 ± 11% collection efficiency at up to 3000 μg HNO_3. Nylon filters from Millipore Corp. and Ghia Corp. were shown to be equal for HNO_3 sampling.

Clean Teflon prefilters retained negligible amounts of HNO_3 with or without heating. However, prefilters loaded with atmospheric particulate matter retained up to 25% of HNO_3 at 300 to 500 $\mu g/m^3$ concentration, the retention increasing with the particulate matter loading. Heating decreased but did not eliminate the observed retention. The HNO_3 retained on the prefilter represents a positive error in particulate nitrate measurement by filter collection. However, a loss of atmospheric HNO_3 by collection on the prefilter may not be observable in atmospheric sampling because of a compensating error; dissociation of NH_4NO_3 on inert prefilters and loss as HNO_3 might more than compensate for atmospheric HNO_3 retention. Such dissociation is probably repressed in laboratory trials with constant, elevated levels of HNO_3.

Loss of NH_4NO_3 from Teflon filters by volatilization into a stream of clean air (with collection of HNO_3 on a reactive after-filter) was shown to be important. At 21°C, an average of 45% nitrate loss was observed in six hours at 20 Lpm with filters initially loaded with about 200 μg NO_3^-. A lower limit dissociation constant value of 22 $(ppb)^2$ was determined. Such loss yields positive errors in HNO_3 sampling by the Okita and Spicer procedures but negative errors in particulate nitrate. Loss of NH_4NO_3 from Teflon filters was also demonstrated by reaction with H_2SO_4 aerosol and with gaseous HCl. With H_2SO_4 at an H^+/NO_3^- equivalents ratio of 1.4, nitrate loss of about 95% was observed in six hours in a stream of clean air at 90% R.H.

Loss of nitrate by NH_4NO_3-HCl reaction has not been previously reported. Two hour exposures of 100 ± 20 μg NH_4NO_3 to air containing about 20 ppb HCl at 50% R.H. caused ca. 90% loss of nitrate compared to 18% by volatilization under these conditions. Atmospheric levels of HCl in U.S. cities have not been reported but may be similar to values found in coastal cities in Japan ($\leq$ 8 ppb). Thus nitrate reaction with HCl may be another source of negative error in particulate nitrate and positive error in HNO_3 measurement by dual filter methods.

Laboratory evaluation of the potential nitrate reference sampler included measurement of the efficiency of the denuder for HNO_3 removal and the extent of particulate nitrate loss in the denuder. The denuder was shown to remove, on average, 88% of gaseous HNO_3. No loss of 0.1 to 0.4 μm or 2 ± 1 μm particles of NH_4NO_3 was measurable in the denuder. However, loss of $\geq$ 3 μm nitrate particles by impaction might still be a significant source of error. This could not be directly evaluated.

A dual channel Monitor Labs model 8840 E chemiluminescent NO_x analyzer was converted to measure HNO_3 by difference between NO + NO_2 + HNO_3 on one channel and NO + NO_2 on the second. Response of the sampler to pure HNO_3 was about 10% below that with NO. The limit of detection was estimated to be 6 ppb. A substantial lag time was observed in response to variation in the HNO_3 levels apparently due to conditioning of the tubing. Further improvements are needed to decrease the limit of detection and improve the response rate before its routine use can be recommended.

Nitric acid measurements by the modified chemiluminescent NO_x analyzer were compared to those by filter collection (Okita Method) and to nitric acid by the difference method, TIN-PN, using laboratory-generated HNO_3. When corrected for the 12% HNO_3 penetration through the denuder, results for the three methods agreed within 11%. Without correction, agreement was within 17%. The presence of particulate matter on the prefilter caused the Okita method results to be 13 to 18% below those of the other methods, reflecting HNO_3 retention on the particulate matter.

Atmospheric sampling was done at Lennox and Claremont, California in the South Coast Air Basin. Lennox was chosen because of its expected elevated H_2SO_4 levels while high nitrate levels were expected at Claremont. Sampling techniques included all described above except the chemiluminescent HNO_3 analyzer which was not then available. In addition, sampling for NH_3 was done using a lo-vol filter sampler with a glass fiber prefilter (pH = 7.6) and an oxalic acid-impregnated after-filter. Sampling for H_2SO_4, H^+ and other aerosol constituents employed short term respirable hi-vol filter samples on acid-washed quartz filters (without NH_3 denuder) in addition to the lo-vol sampler previously described.

At Lennox H_2SO_4 concentrations up to 11 $\mu g/m^3$ were observed with the hi-vol sampler, the first report of substantial H_2SO_4 levels in California ambient air. This compares to California's 24-hour standard of 25 $\mu g/m^3$ for total water-soluble $SO_4^=$. Particulate acidity values appeared to represent H_2SO_4, NH_4HSO_4 and adsorbed (or dissolved) HNO_3. Eight-hour lo-vol filter samples had low H_2SO_4 recoveries but H^+ values up to nearly 11 $\mu g/m^3$ (expressed as $SO_4^=$), consistent with the conversion of H_2SO_4 to NH_4HSO_4, a strong acid, on the filter. Short term sampling and low temperature sample storage appeared to be useful in maximizing H_2SO_4 recovery. The dependence of H_2SO_4 levels on wind direction at Lennox suggested stationary emissions as the source of the observed H_2SO_4.

Glass fiber 47 mm diameter filters sampling 2 to 8 hours at 25 Lpm were shown to approximate total inorganic nitrate (TIN) samplers, collecting both atmospheric particulate nitrates and nitric acid. The latter represented, on average, about half of the TIN. Nitric acid was the only observable contributor to artifact particulate nitrate with glass fiber filters.

Heating of filter samplers for atmospheric particulate nitrate and HNO_3 caused increased error and is not recommended. Even without artificial heating, > 50% loss of PN from Teflon prefilters occurred under warm and

dry ambient conditions with corresponding positive error in HNO_3 measurement. Such loss and positive error appear to dominate over HNO_3 retention on the prefilters, which were changed at 2 to 8 hour intervals to minimize particulate loadings. Under conditions of high particulate acidity, evidence of acid-induced nitrate loss was also found.

Atmospheric nitric acid values were compared to those by simultaneous Fourier transform infra-red measurements. Results by the difference method were, on average, high by 20%, but were substantially more accurate than those by simple filter collection techniques. The 12% penetration of HNO_3 through the acid gas denuder was more than offset by an opposing source of error, possibly loss of > 3 μm PN in the denuder. Nevertheless, sampling of PN with an acid-gas denuder led to improved sampling accuracy, especially at high ambient temperature, relative to nitrate sampling with a Teflon filter.

Aside from volatilization of nitrate from the prefilters, simultaneous HNO_3 and NH_3 measurements and the temperature dependence of the calculated dissociation constant support the significance of an equilibrium of these gases with solid NH_4NO_3 in the atmosphere. Observed diurnal variations of particulate nitrate (e.g., morning maxima) and HNO_3 may be more influenced by the effects of changing temperature and NH_3 levels than on the kinetics of NO_x to HNO_3 conversion.

Principal conclusions from the current study are as follows:

1. Atmospheric H_2SO_4 in California's South Coast Air Basin can be determined by short term (2 to 8 hour) sampling with acid-washed quartz fiber filters, low temperature storage of samples in air-tight containers, selective extraction with benzaldehyde and quantitation as $SO_4^=$ by the AIHL microsulfate method.

2. Levels of H_2SO_4 up to 11 $\mu g/m^3$ were observed at Lennox probably due to nearby emissions of H_2SO_4 and/or SO_3. Adsorbed or dissolved HNO_3 probably contributes to the particulate acidity measured by titration.

3. An NH_3 denuder is not essential for sampling atmospheric H_2SO_4.

4. Particulate nitrate sampling with inert filters yields results which are frequently only a small fraction of the true value because of dissociation of NH_4NO_3 and loss of the resulting HNO_3. In addition, other strong acids (e.g., H_2SO_4) can cause substantial nitrate loss. If present, gaseous strong acids (e.g., HCl) will also cause negative errors in particulate nitrate.

5. Nitric acid values obtained by dual filter techniques (e.g., the Okita and Spicer procedures) are typically too high because of particulate nitrate loss from the prefilter.

6. Particulate nitrate (PN) results obtained with an acid gas denuder which removes HNO_3 are substantially more accurate than those obtained

by sampling with inert filters under conditions of high ambient temperature and low R.H.

7. Nitric acid results obtained as the difference between total inorganic nitrate (TIN) and PN are more accurate than these by the dual filter procedures, but average about 20% too high relative to a long path infra-red technique. Loss of > 3 μm nitrate particles in the denuder may be the cause of the positive error.

8. Artifact nitrate formation on glass fiber filters corresponded to the collection of essentially all of the atmospheric HNO_3 even at high levels of the acid. Thus it is likely that the nitrate values obtained by the present ARB hi-vol network represent the sum of the particulate nitrate and nitric acid rather than particulate nitrate alone. For samples in the South Coast Air Basin, HNO_3 represented about half of the total inorganic nitrate.

9. Further modifications of the Monitor Labs NO_x analyzer are needed to reduce the limit of detection for HNO_3 as well as the response time.

III. LABORATORY EVALUATION OF TECHNIQUES FOR HNO_3 AND PARTICULATE NITRATE MEASUREMENTS

A. Nitric Acid Sampling with Filters

1. Introduction

The Okita procedure[2] for HNO_3 collection employs a Teflon prefilter to remove particulate matter and an NaCl-impregnated cellulose after-filter to collect the HNO_3, later measured as nitrate. The Spicer procedure[3] differs only in the use of nylon in place of the NaCl-impregnated filter. Filter collection of gaseous HNO_3 is, in principle, subject to error from losses by sorption on the inner walls of the sampler, on the inert prefilter and on the atmospheric particulate matter on the prefilter. Since such sorption might be rapidly reversible, desorption could occur after sampling but before HNO_3 on the prefilter or sampler walls could be recovered by extraction. The effects of heating the sampler to drive any weakly bound HNO_3 to the after-filter was, therefore, evaluated using both clean and atmospheric particulate-loaded Teflon prefilters.

Both Duralon (Millipore Corp.) and Ghia Corp. nylon filters were evaluated. The former are no longer commercially available. Nylon and NaCl-impregnated, Whatman 41 cellulose filters (NaCl/W41) were compared for efficiency with and without filter heating at varying HNO_3 loadings. The influence of extraction conditions was evaluated since any differences observed may relate to the ease of extraction of HNO_3 (as NO_3^-) following collection. As in the preliminary studies[1], nylon filters were extracted in 0.1N NaOH based on findings by Lazrus[4], and NaCl/W41 and Teflon prefilters, in double distilled water.

2. Extraction of HNO_3 from Filters

To evaluate the effectiveness of different extraction procedures, HNO_3 at two levels was collected simultaneously with up to seven filters without using prefilters. Extraction conditions and results are given in Table 1 from which we conclude that, 1) extraction using an Eberbach platform shaker recovers, on average, 35% more nitrate compared to ultrasonic extraction, and 2) no difference is observable between 30 and 60 minutes ultrasonic extraction or between 30 and 60 minutes mechanical shaking.

Table 1

RECOVERY OF HNO_3 BY VARIOUS EXTRACTION PROCEDURES FROM UNHEATED SAMPLERS ($\mu g\ NO_3^-$ PER FILTER)[a,b]

Trial	Filter Type	Solvent	Extraction Device	Time, min	HNO_3 Recovered
A	Duralon (nylon)	0.1N NaOH	ultrasonic bath[c]	30	2198 ± 184
	Duralon (nylon)	0.1N NaOH	ultrasonic bath	60	2160[e]
	Duralon (nylon)	0.1N NaOH	platform shaker[d]	60	2994 ± 161
	NaCl/W41	H_2O	platform shaker	30	2880[e]
B	Duralon (nylon)	0.1N NaOH	platform shaker	30	171 ± 125
	Duralon (nylon)	0.1N NaOH	platform shaker	60	146 ± 23
	Duralon (nylon)	0.1N NaOH	ultrasonic bath	30	118[e]
	NaCl/W41	H_2O	platform shaker	60	131 ± 74

a. Two hour sampling at 20 Lpm and 50% R.H. No prefilters were employed. Based on nitrate recovered from NaCl/W41 filters the HNO_3 concentrations were 1200 $\mu g/m^3$ and 55 ± 31 $\mu g/m^3$ for trials A and B, respectively. Except as noted, results are mean values for two filters in parallel.

b. Nylon filters are extracted in 5.0 mL 0.1M NaOH and neutralized with 5 mL 0.1N HCl prior to analysis. NaCl/W41 filters are extracted in 10 mL H_2O.

c. Bransonic Model 42.

d. Eberbach Model 6000.

e. Single trial.

Based on these results as well as independent studies of nitrate extraction in water,[5] 60-minute mechanical shaking was employed for subsequent laboratory and atmospheric samples.

3. Loss of HNO_3 on Prefilters, Particulate Matter and Sampler Walls

If HNO_3 loss by desorption from Teflon prefilters is significant, then samplers lacking prefilters should yield higher HNO_3 recoveries. Indeed preliminary results suggested this to be the case.[1] Additional trials comparing HNO_3 collection with clean and atmospheric particulate-loaded prefilters, with and without a Teflon prefilter, are given in Table 2. Two types of samplers without prefilters were evaluated; one type employed a two-stage, stacked Nuclepore filter holder with the first-stage empty. The second used only a Nuclepore singe-stage filter holder. No filter heating was employed. Comparison of results with these samplers permitted assessment of the significance of air leakage with the two-stage sampler as well as the additional wall losses encountered when a prefilter is used. Results are corrected for the atmospheric particulate nitrate if present (assuming no volatilization of this nitrate from the prefilter during these trials).

Based on ratios of means, average results by the three samplers differed by only ± 3%. Relative to the samplers with prefilters, the ratios of mean results were 0.97 for the two-stage and 1.03 for the single-stage samplers without prefilters. Thus these results do not support the significance of HNO_3 loss by desorption. The retention of HNO_3 on particulate matter observed in these trials will be discussed below.

Okita et al.[2] and Forrest et al.[6] have employed sampler heating to decrease error in HNO_3 sampling. To evaluate the effects of such heating, Teflon prefilters and NaCl/W41 or nylon after-filters were subjected to either continuous heating during sampling at 40°C, or to three minutes sampling clean air at ca. 50°C following HNO_3 collection. Both clean and atmospheric-particulate loaded prefilters were employed. The filter holder inner walls and filter support grid were rinsed to assess HNO_3 losses on these surfaces.

Tables 3 and 4 detail experiments to assess the effects of filter heating, use of a clean or soiled prefilter and extent of wall losses. We conclude from these experiments that 1) as in Table 2, the use of a clean prefilter does not reduce the HNO_3 recovered on the after-filter with or without filter heating, 2) HNO_3 losses to the sampler walls are not significant, 3) particulate matter on the prefilter caused 5.6 ± 0.4% retention of HNO_3 at 50% R.H. and about 30% retention at 80% R.H. in spite of filter heating. (Since the atmospheric nitrate level on the prefilter was only about 3 $\mu g/m^3$, volatilization of this NO_3^- from the prefilter would cause a relatively minor error in the observed HNO_3

Table 2 RECOVERY OF HNO_3 WITH AND WITHOUT TEFLON PREFILTERS USING UNHEATED NaCl/W41 SAMPLERS[a]

Trial	Temp °C	R.H. (%)	Prefilter	Prefilter Loading, µg	HNO_3 Recovered, µg/m³ as NO_3^- Prefilter	After-Filter	Σ[b]
	32	30	None[c]	None	-	300	300
16C	32	30	None[d]	None	-	244	244
	32	30	Zefluor[e]	None	1.3 ± 0.1	240 ± 14	244 ± 14
	32	30	None[c]	None	-	193	193
16D	32	30	None[d]	None	-	256	256
	32	30	Zefluor[e]	271 ± 87	7.0 ± 4.4[f]	235.0 ± 0.5	242 ± 4.4
	21	50	None[c]	None	-	211	211
16E	21	50	None[d]	None	-	255	255
	21	50	Zefluor[e]	None	2.2 ± 0.1	236 ± 14	238 ± 14
	21	50	None[c]	None	-	207	207
16F	21	50	None[d]	None	-	210	210
	21	50	Zefluor[e]	768 ± 5	39.6 ± 1.5[g]	174 ± 1	214 ± 2

a. All trials are approximately four hours at 20 Lpm.

b. Based on the recoveries in preceding trials, washing of filter holders was omitted.

c. A two stage Nuclepore stacked filter holder was used with the first stage empty.

d. A single-stage Nuclepore filter holder was used.

e. 2.0 µm pore size Ghia Corporation Teflon filters.

f. Corrected for the 1.0 µg/m³ NO_3^- contributed by the atmospheric particulate matter.

g. Corrected for the 6.1 µg/m³ NO_3^- contributed by the atomspheric particulate matter.

Table 3

Loss of HNO_3 on Prefilters, Particulate Matter and Sampler Walls[a]

Exp. No.	Relative Humidity %	Teflon Prefilter Loading	After-Filter	Heating Technique	HNO_3 Recovered, $\mu g/m^3$ as NO_3^- Prefilter	After-Filter	Holder	Σ
2	50	clean	NaCl/W41	post[b]	< 4.0	253 ± 53	10 ± 6.2	265 ± 53
	50	atm. particulate[c]	NaCl/W41	post	15 ± 1.2[d]	254 ± 4	4.7 ± 0.4	274 ± 4
	50	clean	NaCl/W41	contiruous[e]	< 3.6	262 ± 2	12 ± 15	276 ± 15
	50	clean	NaCl/W41	none	< 3.6	274	7.3	283
3	50	clean	Duralon[f]	post	< 4.0	214 ± 4	5.5 ± 2	222 ± 4
	50	clean	Duralon	contiruous	< 4.0	220	5.7	228
	50	clean	NaCl/W41	post	< 3.7	238 ± 42	33 ± 17	273 ± 45
	50	atm. particulate[c]	Duralon	contiruous	12[d]	222	3.3	237
4	80	clean	Duralon	contiruous	< 3.8	190 ± 8	2.9 ± 0.3	195 ± 8
	80	atm. particulate[g]	Duralon	contiruous	29 ± 4[d]	177 ± 8	3.3 ± 0.4	209 ± 17
	80	atm. particulate[g]	Duralon	post	32[d]	157	9.9	200
	80	clean	NaCl/W41	post	< 3.7	229 ± 8	9.6 ± 1	240 ± 8
5a	50[h]	clean	NaCl/W41	post	0.4 ± 0	308 ± 42	4.2 ± 1.0	313 ± 42
	50[h]	no filter	NaCl/W41	post	---	343	3.5	347
5b	80[h]	clean	NaCl/W41	post	0.7 ± 0.4	236 ± 2	5.1 ± 1	242 ± 2
	80[h]	no filter	NaCl/W41	post	---	237	3.7	241

a. Except as noted, two-hour sampling at 20 Lpm with 47 mm filters. Prefilters are 1 μm pore size Zefluor filters (Ghia Corp.).
b. Ambient air heated to ca. 50°C passed through sampler at 20 Lpm for 3 minutes.
c. Filters pre-loaded with 10 m^3 air samples in Berkeley containing 3.3 ± 0.4 $\mu g/m^3$ NO_3^-.
d. Corrected for atmospheric NO_3^-.
e. Sampler heated continuously at 40°C during sampling.
f. Nylon filters supplied by Millipore Corp.
g. Filters pre-loaded with 10 m^3 air samples in Berkeley containing 2.8 ± 0.4 $\mu g/m^3$ NO_3^-.
h. Six-hour sampling.

Table 4

The Effects of Heating on HNO_3 Recovery with Clean and Particulate Loaded Prefilters[a]

Prefilter	After-Filter	Heating Procedure	Nitric Acid Recovered $\mu g/m^3$ as NO_3^- Prefilter[b]	After-Filter	Holder	Σ
Atm. particulate on 2 μm Zefluor	Duralon	none	86.6	226	7.1	320
"	Duralon	post	83.1	140	7.1	230
Atm. particulate on 1 μm Zefluor	Duralon	none	50.4	231	9.8	291
"	Duralon	continuous	41.4	174	4.7	220
"	Duralon	post	50.2	158	8.9	217
Clean 2 μm Zefluor	NaCl/W41	none	< 2.1	62.3 ± 7.2	8.4 ± 5.7	73 ± 9.2[c]
"	NaCl/W41	post	< 2.1	66.4 ± 0.1	7.2 ± 0.1	75.2 ± 0.1[c]
"	Duralon	none	< 2.1	53.1	9.0	63.2

a. Two-hour sampling at 50% R.H., 20 Lpm.

b. Results corrected for atmospheric nitrate with particulate loaded filters.

c. In these trials an additional NaCl/W41 filter behind the after-filter was used which collected ca. 1 $\mu g/m^3$ HNO_3 as NO_3^-. The summations include these values.

retention), and 4) with heated samplers using nylon after-filters, recovery of HNO_3 was reduced in some cases by up to 25%. The source of this loss and its variability will be discussed in Section 4 below.

In Tables 2 through 4, the level of HNO_3 retained by the particulate matter on the prefilters varied depending on particulate loadings and exposure conditions. The relationship between TSP loadings on the prefilter and HNO_3 retention with heated and unheated samplers is shown in Figure 1. With high TSP, > 20% retention is observed. It should be noted that with prefilters bearing relatively high particulate nitrate levels, volatilization of ammonium nitrate by dissociation to HNO_3 may more than offset HNO_3 retention. Under such conditions heating the samplers may aggravate this source of positive error in HNO_3 measurement. However, such sources of positive error in HNO_3 are probably repressed during these laboratory trials since the presence of a continuous, relatively high HNO_3 level should hinder dissociation of NH_4NO_3. Positive errors in HNO_3 measurement are more likely to be observed in atmospheric sampling. Frequent filter changes are desirable to minimize both positive and negative error in HNO_3 measurement.

The nitrate values on nylon and NaCl/W41 filters in Tables 2, 3, 4 permit assessment of the precision of sampling HNO_3 in the concentration range 60 to 300 $\mu g/m^3$. The median C.V. for trials in which two or more values were averaged was 3.5% for NaCl/W41 (n = 13, range 0.1 to 21%) and 4.4% for Duralon nylon (n = 4, range 1.9 to 6.8%).

4. The Efficiency of Nylon and NaCl-Impregnated Filters for HNO_3 Collection

The efficiency of post-heated nylon and NaCl/W41 for HNO_3 collection at high HNO_3 loadings was determined by sampling with two filters of the same type in series, and with nylon followed by NaCl/W41, as shown in Table 5. All trials were for six hours during which 1700-2600 µg of HNO_3 was sampled. Based on the proportion of HNO_3 retained on the initial filter, NaCl/W41 filters were 97 ± 1% efficient at 50 and 80% R.H. With a Duralon front filter and NaCl/W41 after-filter, the total recovered HNO_3 was reduced by 16 to 40% suggesting unidentified losses in spite of post-heating the sampler. With two nylon filters in series, 30-50% of the HNO_3 was on the after-filter. This implies relatively low efficiency for these filters, consistent with the low total recovered HNO_3 in these samplers. To obtain efficiencies for nylon filters, the HNO_3 retained on nylon front filters was compared to the HNO_3 retained by the NaCl/W41 front filter sampling in parallel. The latter was corrected for the 3% penetration.

The results indicate that at high HNO_3 loadings, post-heated nylon filters are only about 33% efficient at 50% R.H. and about

Figure 1

RETENTION OF HNO_3 ON ATMOSPHERIC PARTICULATE MATTER
(300-500$\mu g/m^3$ HNO_3)

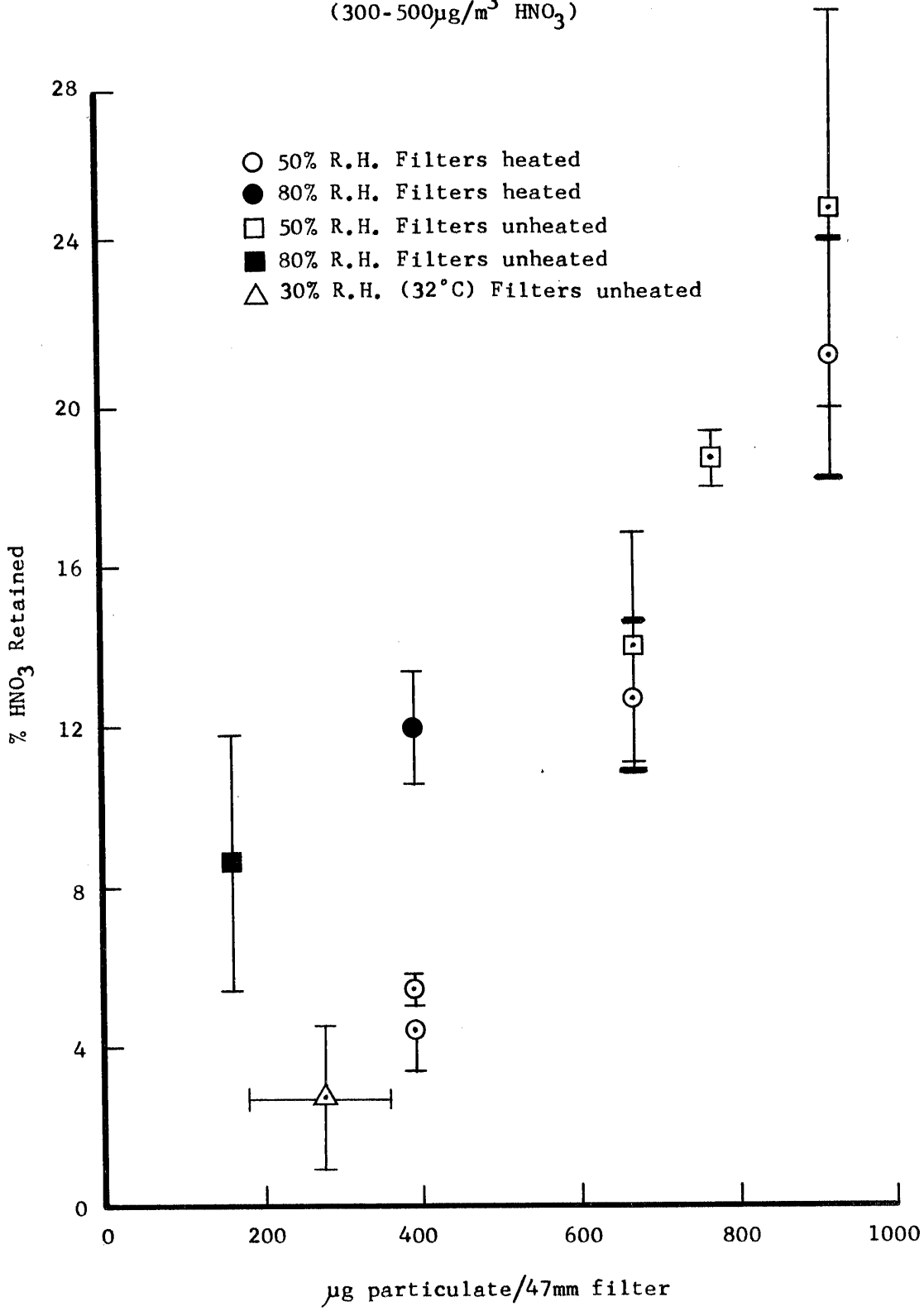


Table 5

Efficiency of Post-Heated[a] Filters for HNO_3 Collection[b]

R.H.(%)	Front Filter	After-Filter	HNO_3 Recovered, $\mu g/m^3$ as NO_3^-				Front Filter Efficiency, %
			Front Filter	After-Filter	Holder	Σ	
50	NaCl/W41	NaCl/W41	341	3.6	1.9	347	98.3[c]
50	Duralon	NaCl/W41	109	95.4	4.5	209	31.0[d]
50	none	NaCl/W41	---	343	3.5	347	---
50	Duralon	Duralon	119	119	3.1	241	33.9[d,e]
80	NaCl/W41	NaCl/W41	210	5.1	2.6	218	96.3[c]
80	Duralon	NaCl/W41	120	60.6	3.4	184	55.5[d]
80	none	NaCl/W41	---	237	3.7	241	---
80	Duralon	Duralon	95.4	46.3	3.6	145	44.1[d,f]

a. See footnote b, Table 3.

b. Six-hour sampling at 20 Lpm with 47 mm filters.

c. The % of the total recovered NO_3^- on the front filter. The mean efficiency at 50 and 80% R.H. is 97.2 ± 1.7%.

d. $$\frac{NO_3^- \text{ on Front Filter (Duralon)}}{NO_3^- \text{ on Front NaCl/W41 Filter} \times \frac{1}{.972}} \times 100$$

e. Using the technique of Smith[12], the overall efficiency for the two filters in series is about zero.

f. Using the technique of Smith[12], the overall efficiency for the two filters in series is about 78%.

50% efficient at 80% R.H. These results contrast with those shown in Tables 3 and 4 implying that the efficiency of nylon filters for HNO_3 varies with the total amount collected, at least when heated samplers are employed. Figure 2 summarized calculated efficiencies observed for Duralon nylon and NaCl/W41 filters at varying HNO_3 loadings and 50-80% R.H.

Efficiencies for heated nylon filters decreased sharply with increased HNO_3 loadings. However at loadings likely to be encountered in ambient air samples, $\leq$ 500 µg HNO_3 as NO_3^-, efficiencies for nylon are $\leq$ 10% below those for NaCl/W41. With unheated nylon filters the mean collection efficiency was 95 ± 11%.

Forrest et al. have noted the decrease in efficiency of NaCl impregnated filters at low R.H., finding about 50% efficiency at 25% R.H.[13] To assess the effect of humidity, unheated NaCl/W41 filters were evaluated for efficiency at < 2% R.H. With three trials at 285 µg/m^3, on average, only 55% of the HNO_3 retained by two NaCl/W41 filters in series was on the front filter. Using the technique of Smith,[12] the overall sampler efficiency for the two filters in series is about 40%. In general, these results are not significant for atmospheric sampling but may influence laboratory applications of these filters as HNO_3 samplers.

Since Duralon filters are no longer commercially available, an alternative nylon filter supplied by Ghia Corp. was compared to Duralon as shown in Table 6. The results indicate no significant difference in efficiency between the two filter types.

5. Summary and Conclusions

a. HNO_3 sampling with heated nylon filters yields low results because of reduced efficiency especially for high HNO_3 loadings. Unheated nylon and NaCl/W41 filters with or without heating are $\geq$ 95% efficient independent of HNO_3 levels. These results are consistent with HNO_3 retention on nylon by physical adsorption and on NaCl/W41, by chemical reaction (e.g., $NaNO_3$ formation with liberation of HCl).

b. Ghia and Duralon nylon filters are not significantly different for HNO_3 sampling.

c. Losses of HNO_3 up to 25% were found on particulate matter on the prefilter. The losses were highest with unheated samples at high R.H.

d. Heating filter samplers reduced loss of HNO_3 on soiled Teflon prefilters significantly. Heating may, however, aggravate positive errors in atmospheric HNO_3 measurement by volatilization of NH_4NO_3 from the prefilter.

Figure 2

HNO_3 COLLECTION EFFICIENCY OF NYLON AND NaCl-IMPREGNATED FILTERS
(50-80 % R.H.)

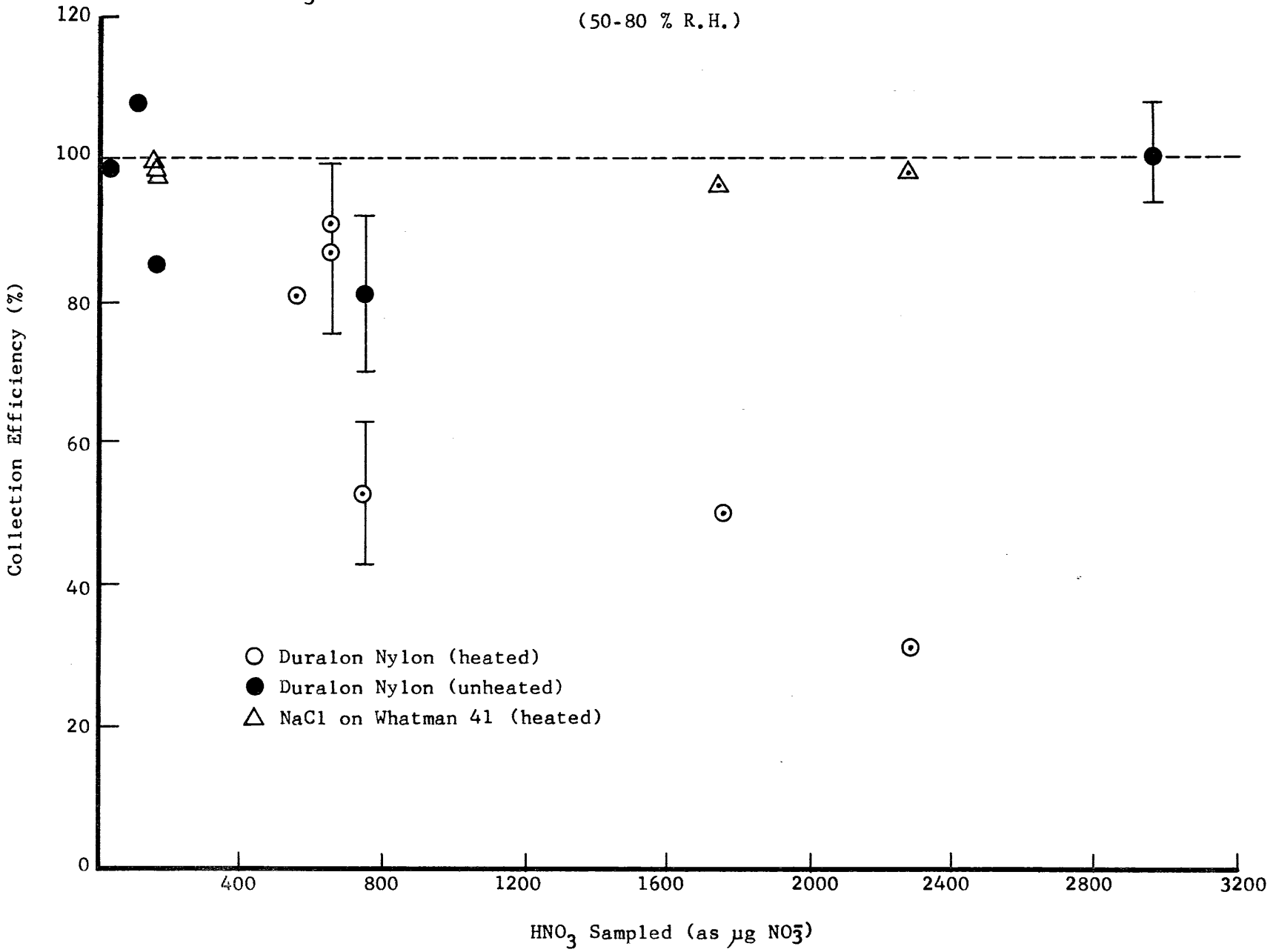


Table 6

Comparison of Duralon and Ghia[a] Nylon Filters for HNO_3 Collection

HNO_3 Sampled (as μg NO_3^-)	Ghia Nylon/Duralon
684[b,c]	1.13
1368[c,d]	0.96
1699[b,e]	1.00
3398[d,e]	0.99
	Mean: 1.0 ± 0.1

a. Ghia Corp., Pleasanton, California.

b. 10 Lpm.

c. 50% R.H.

d. 20 Lpm.

e. 80% R.H.

e. Since volatilization of NH_4NO_3 from the prefilter will yield lower apparent HNO_3 loss, the observed loss of HNO_3 to particulate matter is expected to vary with the nitrate content of the particulate matter.

B. Negative Errors in Particulate Nitrate Filter Sampling

1. Introduction

As discussed in the preceding section, HNO_3 is retained by particulate matter on inert prefilters representing a source of positive error in determining particulate nitrate by conventional filter collection. Such error may, however, be more than offset by losses of particulate nitrate from the prefilter producing a corresponding positive error in HNO_3 measurement by collection on an after-filter. Such loss of particulate nitrate can result from volatilization of nitrate salts or by reaction of such salts with gaseous or particulate strong acids.

2. Volatilization of Ammonium Nitrate

To evaluate losses due to volatilization, air free of particulate nitrate and HNO_3 was passed through filters loaded with about 200 μg < 0.5 μm particle size NH_4NO_3 at 20 Lpm for six hours. Both the decrease in nitrate on the loaded filter and the increase in nitrate on NaCl/W41 after-filters downstream of the loaded filter were measured. The results of trials at 50% and 80% R.H. are shown in Table 7. At 50% R.H. excellent agreement was observed between the techniques; both indicated close to 60% loss of nitrate to the air stream. At 80% R.H., the 50% NO_3^- loss, by difference, compares to 33% based on the NO_3^- collected on the after-filter. Nitrate losses to the inner surfaces of the filter holder may account for some of this difference. Such losses were not measured, however. On average, the loss of NH_4NO_3 appears to decrease at higher R.H.

These results suggest that volatilization of NH_4NO_3 can be a major source of negative error in sampling particulate NO_3^- with Teflon filters. This must result in a corresponding positive error in HNO_3 measurements by the nitrate collected on after-filters. However, the presence of relatively high NH_3 and HNO_3 levels in ambient air may decrease this error relative to that in Table 6, while elevated temperatures should increase it.

These data permit estimation of the equilibrium constant for NH_4NO_3 dissociation:

$$NH_4NO_3 \rightleftarrows NH_3 + HNO_3 \qquad K = (NH_3)(HNO_3)$$

Based on a mean loss of 45 ± 11%, K is $\geq$ 22 $(ppb)^2$. Since the air

Table 7

Loss of < 0.5 μm NH_4NO_3 Particles from Teflon Filters into a Clean Air Stream (μg NO_3^-/filter)[a,b]

Relative Humidity,%	Initial NH_4NO_3 Loading	Final NH_4NO_3 Loading	Calculated Nitrate Loss	NO_3^- on After-Filter[c]	Mean % Loss[e]
50	190 ± 8[d]	76.5 ± 4.1	113.5 ± 9	109 ± 10.2	58.6 ± 1.7
80	180 ± 7[d]	90.0 ± 5.7	90.0 ± 11	59.9 ± 5.3	42 ± 12

a. Contaminant particulate nitrate and HNO_3 were removed from the air stream by two NaCl/W41 filters in series ahead of the NH_4NO_3-loaded 1 μm Fluoropore filters.

b. Sampling of purified air was for six hours at 20 Lpm and 21 ± 1°C. Except as noted results are mean values for two trials.

c. An NaCl/W41 after-filter collected the nitrate lost from the loaded Teflon filter.

d. Initial loadings based on analysis of one of three filters loaded simultaneously with NH_4NO_3. Earlier studies indicated loadings should be equivalent for the three filters with a C.V. of 2%. The precision of the analytical method is ca. 3%. Accordingly the precision of the initial loading is estimated at 4%.

e. Based on both calculated NO_3^- loss and NO_3^- on after-filter.

stream may not be saturated on passing through the loaded filters, this is a lower limit value. It compares to the value ca. 10 (ppb)[2] at 20°C for pure NH_4NO_3 based on extrapolated dissociation pressure values.[7]

3. Loss of Nitrate by Reactions with Gaseous and Particulate Acids

Loss of nitrates from inert prefilters may result from reaction of any nitrate salt leading to HNO_3 formation. Reactions of NH_4NO_3 with gaseous and particulate strong acids were evaluated since this salt may often be the dominant nitrate form present in atmospheric particulate matter. The reactions considered include:

a. $NH_4NO_3(s) + HCl(g) \rightarrow NH_4Cl(s) + HNO_3(g)$

$$\Delta F_{298°K} = +1.98 \text{ Kcal/mole}^2$$

$$K_{298°} = 3.53 \times 10^{-2}$$

b. $2NH_4NO_3(s) + H_2SO_4(l) \rightarrow (NH_4)_2SO_4(s) + 2HNO_3(g)$

$$\Delta F_{298°K} = +4.14 \text{ Kcal/mole}^2$$

$$K_{298°} = 9.21 \times 10^{-4}$$

Loss of NO_3^- by reaction with H_2SO_4 has been previously observed or inferred.[8,9] The reaction is irreversible under conditions in which HNO_3 is permitted to escape. Based on standard free energy of formation calculations[10] neither reaction is favored thermodynamically. However, under conditions in which the equilibrium concentration of HNO_3 is not permitted to build up (e.g., in a moving stream of air passing through a filter loaded with NH_4NO_3 particles), NH_4NO_3 loss might still occur.

To evaluate the loss of NH_4NO_3 with gaseous HCl, ammonium nitrate particles of $\leq$ 0.2 μm diameter particle size were generated with a nebulizer system previously described.[11] Particles in the range $\geq$ 0.1 μm were measured with a Royco Model 226 optical particle counter.

Teflon filters loaded with 80-130 μg of the salt (as NO_3^-) were exposed for two hours to clean air or to about 20 ppb HCl in air at 50% R.H. The HCl concentration was established with bubbler samples collected in 0.01M NaOH and analyzed by a colorimetric procedure using mercuric thiocyanate.[14] Other conditions and results are summarized in Table 8. In the absence of HCl, the nitrate loss due to volatilization was about 18%, which compares to 19.5 ± 0.3% calculated from Table 7 assuming a constant loss

Table 8

PERCENT LOSS OF NH_4NO_3 FROM TEFLON FILTERS BY REACTION WITH HCl IN AIR AT 50% R.H.a,b

Mean NH_4NO_3 Loadings ($\mu g\ NO_3^-$/filter)	% Loss at HCl level		
	0	17 ± 1 ppb	23 ± 1 ppb
128	18.1 ± 0.7	87 ± 4	
80			90 ± 8

a. 0.2 ± 0.1 μm NH_4NO_3 particles on 47 mm, 2 μm pore size Zefluor filters. Flow rate = 20 Lpm, T = 21 ± 1°C. Sampling time = 2 hours.

b. Results are mean values for two filters run side-by-side.

rate with time. When 17 to 23 ppb HCl was added, the nitrate loss increased to about 90% of the particulate nitrate sample. Thus the effect of HCl on nitrate loss from Teflon filters was dramatic.

Few data on atmospheric HCl levels are available. Existing data indicate levels up to about 8 ppb with highest values in seacoast cities.[15] HCl at or above this level are possible for many areas in California and might, therefore, profoundly influence particulate NO_3^- values obtained in sampling with inert filters.

To evaluate nitrate loss due to H_2SO_4 reactions employing Teflon filters previously loaded with NH_4NO_3, H_2SO_4 aerosol ($\leq$ 0.1 μm) was added using the generator previously described.[11] Loading time to add about 100 μg H_2SO_4 was ten minutes. The R.H. during H_2SO_4 loading was $\leq$ 1%. Loss of NO_3^- during and subsequent to H_2SO_4 loading was judged by the NO_3^- collected on NaCl/W41 after-filters. Half of the samples were subject to additional exposure to clean air for six hours at 90% R.H. at flow rates equivalent to that used in atmospheric NO_3^- sampling. Sample loadings and results are summarized in Table 9.

During the ten minutes required to load the H_2SO_4 aerosol, loss of nitrate averaged 9 to 14%, more than twice the loss ascribable to volatilization. When exposed to a clean air stream for an additional six hours at 90% R.H., the loss observed was close to 95%, about three times the loss of NO_3^- observed from filters without H_2SO_4. Thus the reaction of NH_4NO_3 with H_2SO_4 on the filter surface is not immediate at $\leq$ 1% R.H. At 90% R.H., wherein the NH_4NO_3 deliquesces to liquid droplets which are likely to dissolve the H_2SO_4 as well, the reaction is nearly complete after six hours.

We conclude that because of the significance of loss of NH_4NO_3 by volatilization as well as reactions with particulate strong acids (e.g., H_2SO_4) and gaseous strong acids (e.g., HCl) particulate NO_3^- values obtained with Teflon filters represent lower limits to the true NO_3^- levels.

C. A Potential Reference Method for HNO3 and Particulate Nitrate Sampling

1. Introduction

In the preceding sections it was demonstrated that particulate nitrate measurements by collection on inert filters are subject to both positive and negative errors. These lead to the complimentary error in HNO_3 measurements by HNO_3 collection with an after-filter. Nevertheless, the sum of the nitrate retained by the prefilter and an efficient after-filter should equal the total inorganic nitrate (i.e., HNO_3 plus particulate nitrate).

Table 9

Loss of NH_4NO_3 from Inert Filters Due to Reaction with H_2SO_4 Aerosol

	Conditions for H_2SO_4 - NH_4NO_3 Reaction			
	10 min at room temp. ≤ 1% R.H.[c,g]		6 hours at room temp. 90% R.H.[h]	
	Trial I	Trial II	Trial I	Trial II
Initial NO_3^-, µg[a]	101.1 ± 5.4	113.7 ± 2.8	91.9 ± 2.6	71 ± 2.7
Initial H_2SO_4, µg $SO_4^=$[b]	66.5 ± 3.5	63 ± 5	91.2 ± 4.1	89.3 ± 9.6
Nitrate lost by H_2SO_4 reaction, µg[d]	9.0 ± 0.6	15.8 ± 0.4	86.3 ± 0.8[e]	67.0 ± 3.1[e]
Nitrate lost by volatilization, µg[f]	< 5	< 5	29.0	35.1

a. From 0.2 ± 0.1 µm NH_4NO_3 particles.

b. From ≤ 0.1 µm H_2SO_4 particles added following initial loading with NH_4NO_3.

c. Reaction time was the period during which H_2SO_4 was loaded on the filters at a flow rate of 10 Lpm with 47 mm filters.

d. Collected by NaCl-impregnated W41 filters.

e. Includes the NO_3^- lost during 10 min. loading of H_2SO_4 at 1% R.H., and flow rate of 28.3 Lpm.

f. Filters initially contain the NO_3^- level shown above as "initial NO_3^-" but without added H_2SO_4.

g. Initial ratio of equivalents H^+/NO_3^- = 0.77 ± 0.1.

h. Initial ratio of equivalents H^+/NO_3^- = 1.4 ± 0.2. Flow rate 20 Lpm.

R. Shaw et al. recently proposed[16] use of such a total inorganic nitrate (TIN) sampler in parallel with a particulate nitrate sampler as shown schematically in Figure 3. For the latter, the ambient air mixture of HNO_3 and particulate NO_3^- passes first through a diffusion denuder coated on its inner walls with powdered MgO. The relatively rapid diffusion of gases permits removal of HNO_3 (and other acidic gases) while permitting non-volatile particulate matter to penetrate with high efficiency. The nitrate reaching the Teflon prefilter in this case should be true particulate nitrate. The after-filter collects any of this nitrate lost by volatilization or reactions liberating HNO_3. If particulate NO_3^- is not lost in the denuder, the total of the NO_3^- on these two filters equals the total particulate nitrate (PN) in the atmosphere. The difference between TIN and PN should equal the ambient HNO_3 level.

The efficiency of HNO_3 removal in such a denuder, under conditions of laminar flow (Reynolds number < 2000), can be calculated by the Gormley-Kennedy equation:[37]

$$\frac{\overline{C}}{C_o} = 0.82 \exp(-15\Delta) + 0.098 \exp(-89\Delta) + 0.033 \exp(-228\Delta)$$

where $\Delta = DL\pi/4Q$

D = diffusion coefficient (cm^2/sec)

L = total length of tube (cm)

Q = flow rate through tube (cm^3/sec)

C_o = concentration entering tube

$\overline{C}$ = average concentration exiting tube

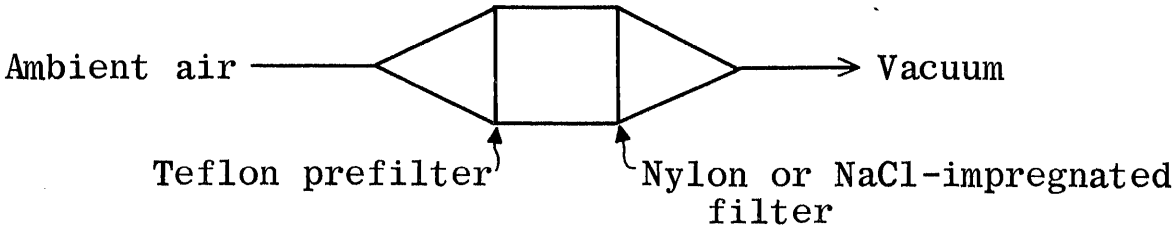
$(1 - \overline{C}/C_o) \times 100$ = percent removal

At the time this work was initiated a diffusion coefficient for HNO_3 was not available. Accordingly, a value of $D = 0.4$ cm^2/sec was employed, as previously used for NH_3. It should be noted that tube diameter is not critical as long as the Reynolds number is maintained below 2000. The most compact denuder configuration consists of an array of parallel tubes, the sum of whose lengths yield the desired total tube length. Based on this value for D, a denuder with eleven, 30 cm tubes should provide > 99% removal of HNO_3 at 20 Lpm (Reynolds number < 500) while removing < 6% of the $\geq$ 0.01 µm particles by diffusion. The data in Section V are based on a denuder of this design. More recently a diffusion coefficient of 0.15 cm^2/sec was measured for HNO_3.[17] With this value and the above equation, the denuder employed for the present work has an expected efficiency for HNO_3 removal of 85.7%.

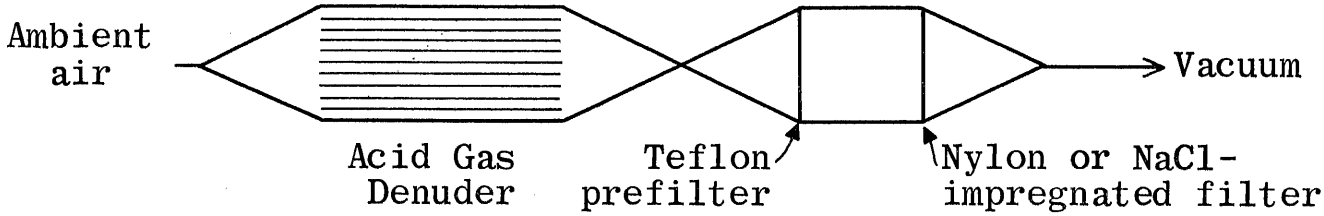
2. Laboratory Evaluation of the Efficiency of the Denuder for HNO_3 Removal

The efficiency of the denuder with eleven, 30 cm tubes was measured by sampling laboratory-generated HNO_3 in parallel with

TOTAL INORGANIC NITRATE (TIN) SAMPLER



PARTICULATE NITRATE (PN) SAMPLER



$$TIN - PN = \text{Ambient } HNO_3$$

Figure 3. SCHEMATIC DIAGRAM OF NITRIC ACID MEASUREMENT BY A DIFFERENCE TECHNIQUE

NaCl/W41 filters. The HNO_3 penetrating the denuder was collected on an NaCl/W41 filter with or without a Teflon prefilter. Figures 7 to 10 (pages 39 to 42) illustrate the design for the trials with both clean and pre-soiled Teflon prefilters. The results summarized in Table 10 indicate that for temperatures in the range 21 to 32°C and relative humidities from 20 to 80%, the efficiency for 85 to 135 ppb HNO_3 averaged about 88%. This result was equal, within experimental error, to that predicted by the Gormley-Kennedy equation employing the measured diffusion coefficient for HNO_3.

Penetration of HNO_3 through the denuder would yield apparent particulate nitrate values which are too high with a corresponding negative error in HNO_3 by difference. Any loss of particulate nitrate in the denuder would produce the reverse. It will be shown in Section V that the expected 12% penetration of HNO_3 through the denuder was apparently more than offset by opposing sources of error in atmospheric sampling.

3. Loss of Particulate Nitrate in the Denuder

The denuder is designed to permit passage of non-volatile particles > 0.01 μm in diameter with high efficiency, based upon losses by diffusion to the walls. However, loss of particulate nitrates may occur by either or both of two additional mechanisms. Relatively large-particle nitrate (e.g., $NaNO_3$) may be lost by impaction near the entrance of the denuder tubes and on the rough MgO coating. In addition, ammonium nitrate, the most likely submicron size nitrate compound in ambient air, might be lost by initial dissociation to gaseous HNO_3 followed by diffusion of HNO_3 to the walls:

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$$

Since the air stream is denuded of HNO_3 by the denuder, dissociation of NH_4NO_3 may be enhanced within and downstream of the denuder tubes.

To measure losses of NH_4NO_3 particles, a nebulizer-type aerosol generator system[1] was employed to prepare NH_4NO_3 particles in the ranges 0.1 - 0.4 μm and 1 - 3 μm. A denuder with eleven freshly prepared 30 cm MgO-coated tubes was employed, oriented vertically. A Royco Model 226 optical particle counter counted particles $\geq$ 0.1 μm. If volatilization was involved in particle loss, loss should be more evident in the smaller particles because their higher surface area per unit mass would increase their volatilization rate. To minimize experimental bias, identical sampling probes and tubing were used upstream and downstream of the denuder.

Table 10 EFFICIENCY VALUES OF DIFFUSION DENUDER FOR 220 - 345 $\mu g/m^3$ (85 - 135 PPB) NITRIC ACID

Trial	Temp. °C	R.H. (%)	Flow Rate, Lpm	Efficiency of HNO_3 Removal, %[a]
5A	21	50	20	97.3
5B	21	80	20	96.9
16C	32	30	20	87.3 ± 2.2
16D	32	30	20	85.6 ± 1.1
16E	21	50	20	85.4 ± 3.3
16F	21	50	20	83.5 ± 0.4
			Overall mean:	87.8 ± 5.1

a. Calculated assuming that all nitrate penetrating the denuder is HNO_3 and the mean TIN values (corrected for atmospheric nitrate, if present) are to equal to the input concentration of HNO_3.

Table 11 summarizes the experimental conditions studied. The average residence time of a particle within a denuder tube at 20 Lpm is 0.3 sec. Both the flow rate and R.H. were varied. However, in all cases the downstream particle count remained equal, within experimental variability, to that upstream for the size ranges 0.1 to 0.2, 0.2 to 0.3 and 0.3 to 0.4 μm. Thus no loss of particles was observed.

In studies with 1 to 3 μm particles, results were obtained both by filter collection and real-time particle counting. The denuder was attached to one of three equivalent positions in the NH_4NO_3 generator system manifold. Nitrate penetrating the denuder was compared to that at the other two positions. Since the airstream penetrating the denuder should be nearly free of HNO_3, dissociation of NH_4NO_3 on an inert filter would be expected. Accordingly, Teflon prefilters and NaCl/W41 after-filters were used at this position.

Because of the limited flow capacity of the NH_4NO_3 generator, the three samplers operated at 10 Lpm rather than the 20 Lpm employed for field sampling with the denuder. However, the average residence time of particles and the air velocity within denuder tubes was maintained approximately equal to that in atmospheric sampling by using 6 denuder tubes in place of the 11 employed in field sampling.

Losses were judged by comparing nitrate levels on the two filters sampling at the manifold with the total NO_3^- on the filters downstream of the denuder. In addition, a Climet Model 206 optical particle counter (OPC) was used for repeated measurements of nitrate particles upstream and downstream of the denuder. The results shown in Table 12 indicate that losses are nil based on filter collection. Similarly, the OPC data showed no difference between upstream and downstream values.

We conclude that loss of 0.1 to 3 μm particulate nitrate in the denuder was not measurable. However, since atmospheric nitrate can be present in particles > 3 μm, and impaction of such particles is likely, loss of particulate nitrate in the denuder cannot be discounted. Unfortunately, the presently available system did not permit experiments with > 3 μm nitrate particles.

D. Modified Chemiluminescent NO_x Analyzer Method

1. Introduction

The dual channel NO_x analyzer, Monitor Labs Model 8840E, relies on the chemiluminescent reaction between NO and ozone to detect and measure NO. In one flow system, NO is measured selectively, while a second flow system reduces NO_2 (and HNO_3) to NO to give

Table 11

CONDITIONS STUDIED FOR LOSS OF 0.1-0.4 μm NH_4NO_3 PARTICLES IN THE ACID GAS DENUDER[a]

Trial	Conditions
1	20 % R.H. 40 Lpm (0.15 sec residence time)
2	20% R.H. 20 Lpm (0.3 sec residence time)
3	60% R.H. 20 Lpm (0.3 sec residence time)
4	60% R.H. 10 Lpm (0.6 sec residence time)

a. The Royco Model 226 OPC provided particle counts in the ranges 0.1-0.2, 0.2-0.3, and 0.3-0.4 μm. Typical particle counts were 150,000, 60,000 and 8,000 per minute for the three ranges.

Table 12

LOSS OF 2 ± 1 μm NH_4NO_3 PARTICLES IN ACID GAS DENUDER

BASED ON PARTICULATE NITRATE COLLECTION[a]

Trial	Nitrate Levels (μg/filter) Upstream	Downstream of Denuder
A	2759 ± 300	2586[b]
B	2774 ± 201	2952[b]

a. Nitrate collected upstream with Zefluor (Teflon) filters. Nitrate collected downstream with a Zefluor and NaCl/W41 in series. The latter retained HNO_3 lost by volatilization from the Teflon filter.

b. The nitrate on the NaCl/W41 after-filter was < 0.1% of the total in 6-minute loading periods.

a measure of total NO_x (Figure 4A). The total NO_x signal minus the NO signal yields the approximate NO_2, since HNO_3 levels are normally small by comparison to NO_2.

The analyzer was modified as described by Joseph and Spicer[18] to provide a continuous measure of atmospheric HNO_3 (Figure 4B). The nylon filter ahead of the second catalyst bed selectively removes HNO_3 but allows passage of NO and NO_2. Thus this channel provides a measure of total NO_x less HNO_3. Since the other channel measures total NO_x (i.e., NO + NO_2 + HNO_3), HNO_3 is measured by the difference signal between the two channels. HNO_3 in ambient air is usually << NO + NO_2, so the difference value is obtained between two relatively large numbers. The modifications made include:

a. installation of an additional NO_x to NO converter, a heated molybdenum catalyst, in what was originally the NO flow system,

b. installation of a 47 mm nylon filter in a glass fiber-filled polypropylene holder (Millipore 43 047 00)* in line ahead of this second catalyst,

c. increasing the temperature of both catalysts' beds from 315°C to 350°C, to increase the efficiency of HNO_3 conversion to NO,

d. moving the flow control orifices ahead of the catalysts and nylon filter to place both flow channels under partial vacuum and thereby minimize HNO_3 losses on surfaces,

e. increasing the sampling rate from 250 mL/min to 720 mL/min for faster response, and

f. increasing the system vacuum from 24 inches Hg to the maximum attainable (28.5 inches Hg), to further minimize HNO_3 loss.

2. Evaluation Procedure

The performance of the modified analyzer was determined with NO, NO_2 and HNO_3. Dilute NO was generated by quantitative dilutions of 5 or 50 ppm NO in N_2 with synthetic air or filtered ambient air. NO_2 was obtained by gas phase titrations of the NO with O_3. HNO_3 concentrations were obtained by quantitative dilution with dry cylinder or filter ambient air of 10 to 40 ppm HNO_3 in dry N_2 from a 30 ft Teflon bag.[1] The concentration of the HNO_3 in the Teflon bag was determined by a nitrate specific electrode following bubbler collection in 0.1N NaOH and adjustment of electrolyte.

---

*Used in place of a Teflon holder employed by Joseph and Spicer.

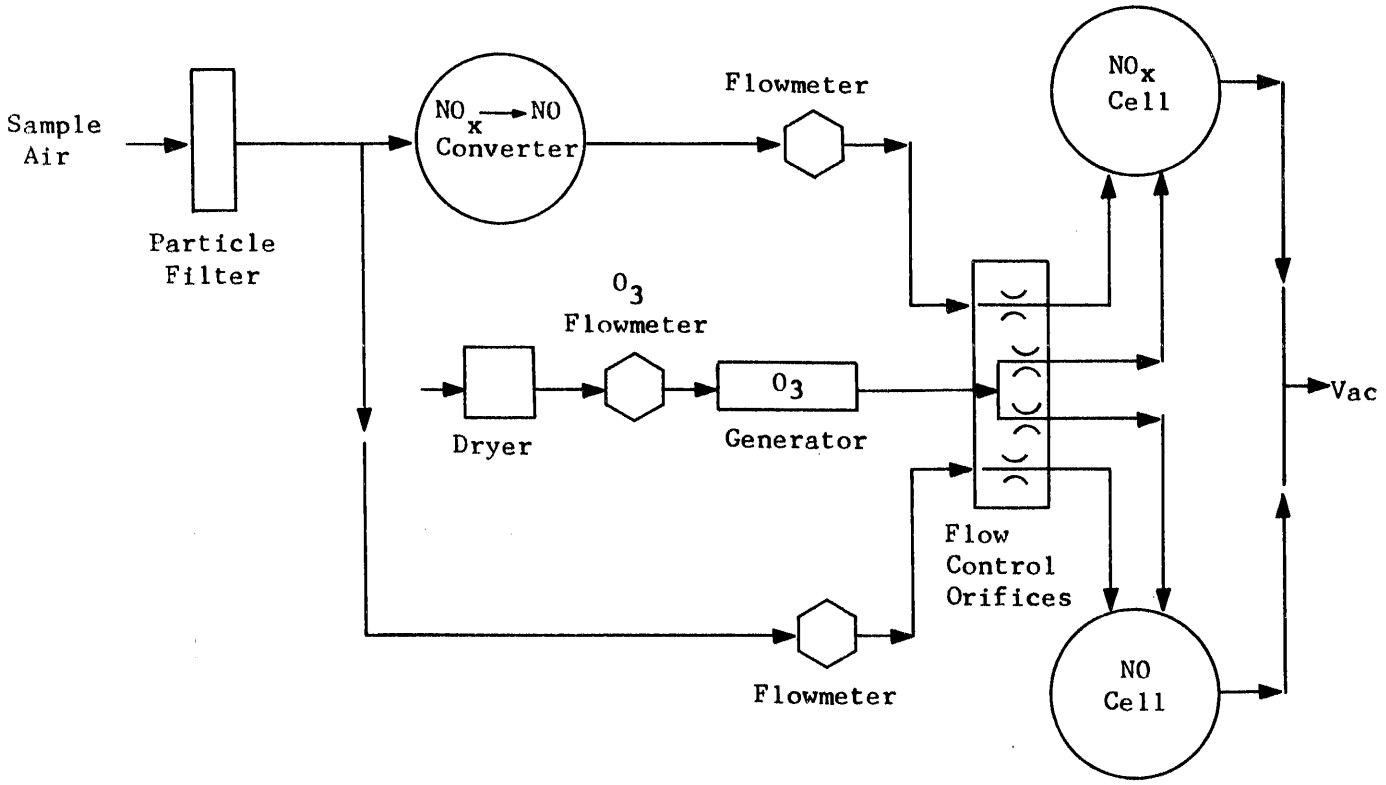


Figure 4A Schematic of Unmodified Monitor Labs NO_x Analyzer.

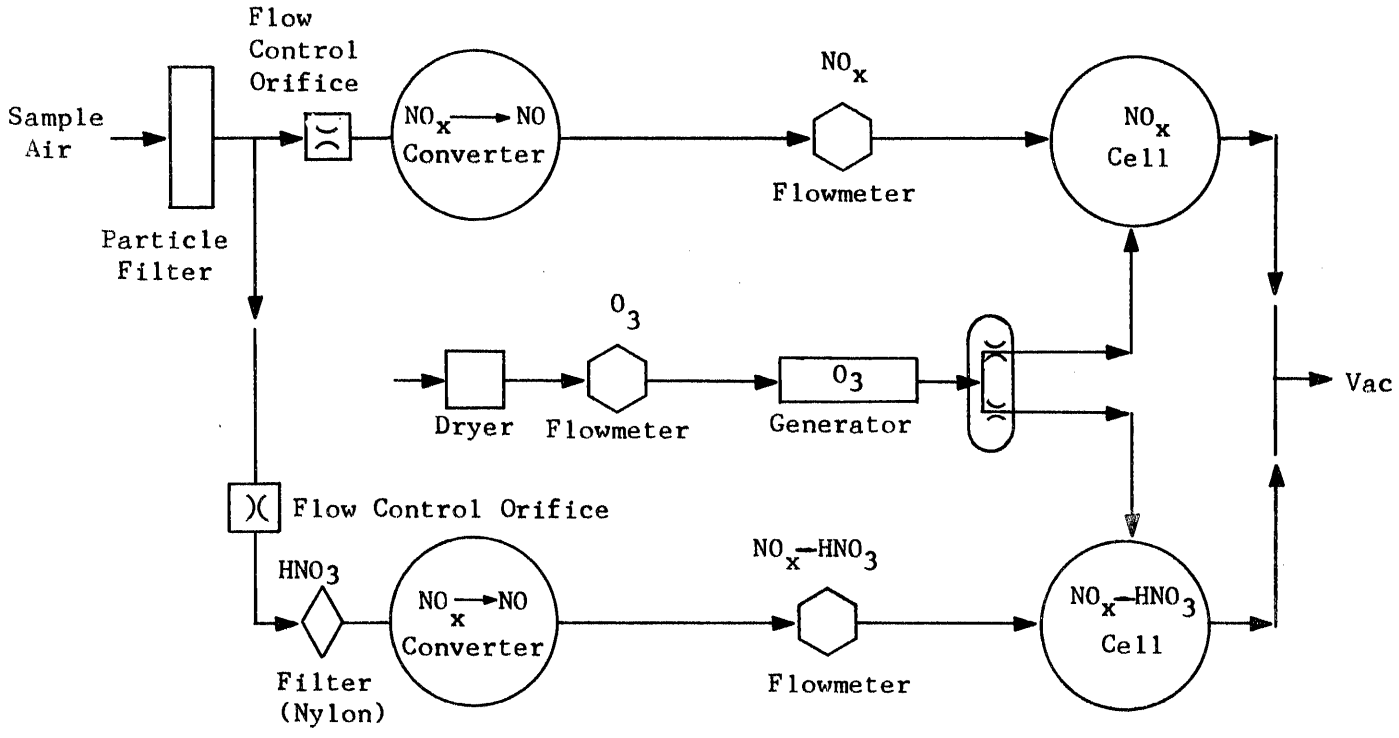


Figure 4B Schematic of Monitor Labs Analyzer Modified For HNO_3 Analysis.

Converter efficiency for NO_2 was evaluated by bypassing each converter, in turn, and adding ozone to the NO stream gas phase titration and looking for changes in the NO_x channel, while the decrease in the NO channel was used to determine the O_3 added.

3. Results

The response of the modified analyzer to NO, NO_2 and HNO_3 are shown in Figures 5 and 6 for NO and HNO_3. The addition of O_3 to the NO resulted in no reduction in NO_x signal until the O_3 concentration exceeded that of NO (56 ppb) indicating 100% conversion in each case. The response of the instrument to HNO_3 in dry air differed from that for NO by about 10% at the upper end of the range.

The lower limit of detection of HNO_3 was estimated to be 6 ppb based on twice the instrument noise. This compares to 1 to 2 ppb presently claimed by Spicer.[19] The instrument's rate of response is a function of the time-constant setting. On the 20 sec setting, the time to 90% of final response to NO and NO_2 was 46 sec. However with HNO_3 at 50 to 60% R.H. an initial lag time of between 0.75 and 8 minutes was observed, increasing with decreasing HNO_3 concentration apparently due to conditioning of the tubing. The time to 90% of final response ranged between 20 minutes to over 1.5 hours varying inversely with concentration.

We conclude that the continuous HNO_3 analyzer, as described here, is a very useful device for laboratory application. However, successful application in the atmosphere must be preceded by additional efforts to decrease the response time and limit of detection to values similar to those reported by Spicer. The higher limit of detection probably reflects the greater electronic noise in the photomultiplier tube. The reason for the greater response time remains unknown.

E. Intermethod Comparison of Techniques for HNO_3 Measurement

1. Objectives

The objectives of this series of experiments were: 1) to compare HNO_3 measurements by the difference technique to HNO_3 by filter collection (the Okita method) and to the modified Monitor Labs chemiluminescent HNO_3 analyzer, and 2) to obtain additional evaluations of the efficiency of the HNO_3 diffusion denuder for HNO_3 removal. Efficiency results from these experiments were discussed in Section III.

Experiments were planned to simulate the meteorological extremes encountered in the atmospheric sampling described in Section V. Experiments employed either clean Teflon (Zefluor) prefilters or Teflon filters preloaded with atmospheric particulate matter to

Figure 5
MONITOR LABS RESPONSE TO NITRIC OXIDE ON 100ppb RANGE

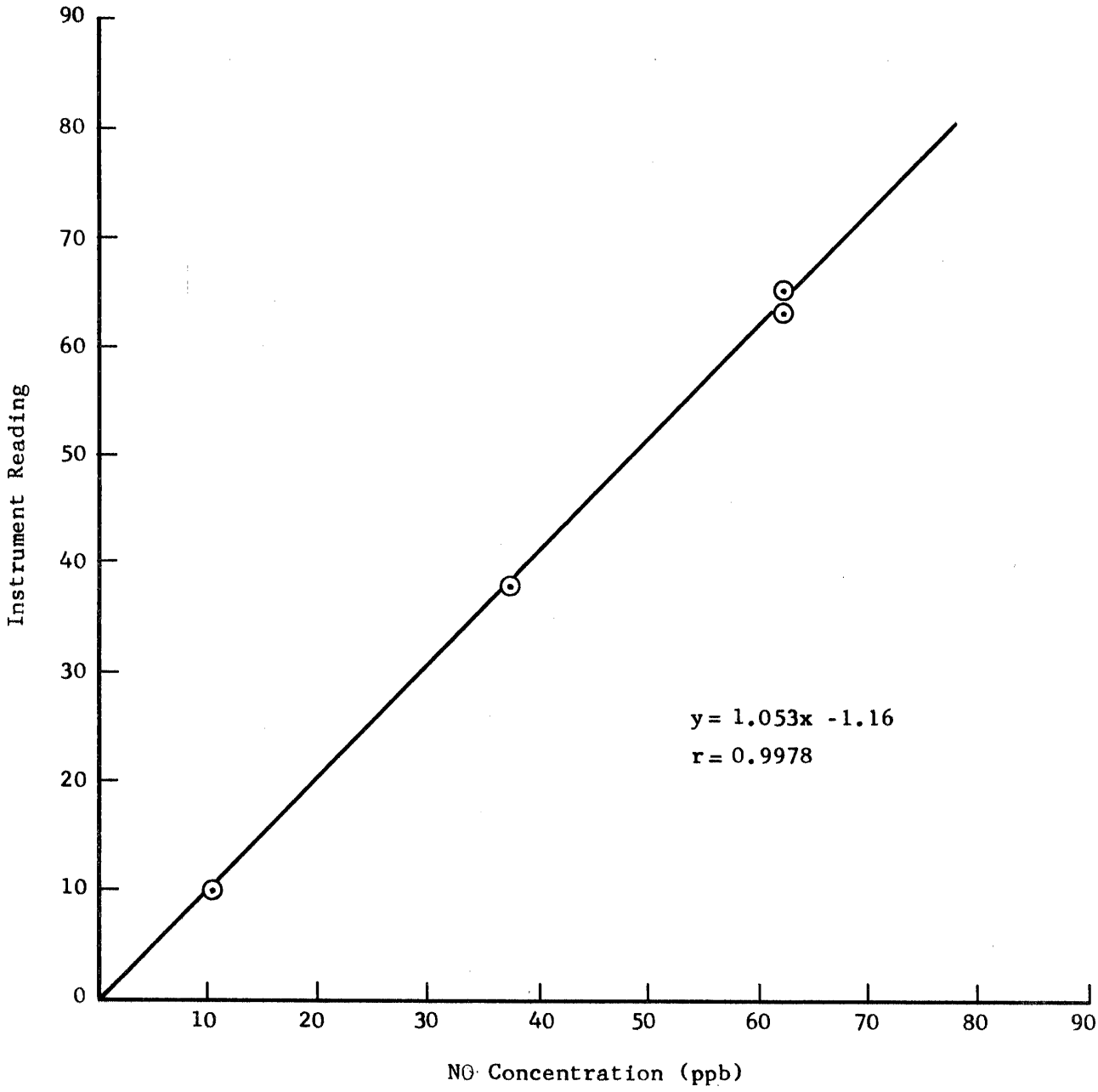
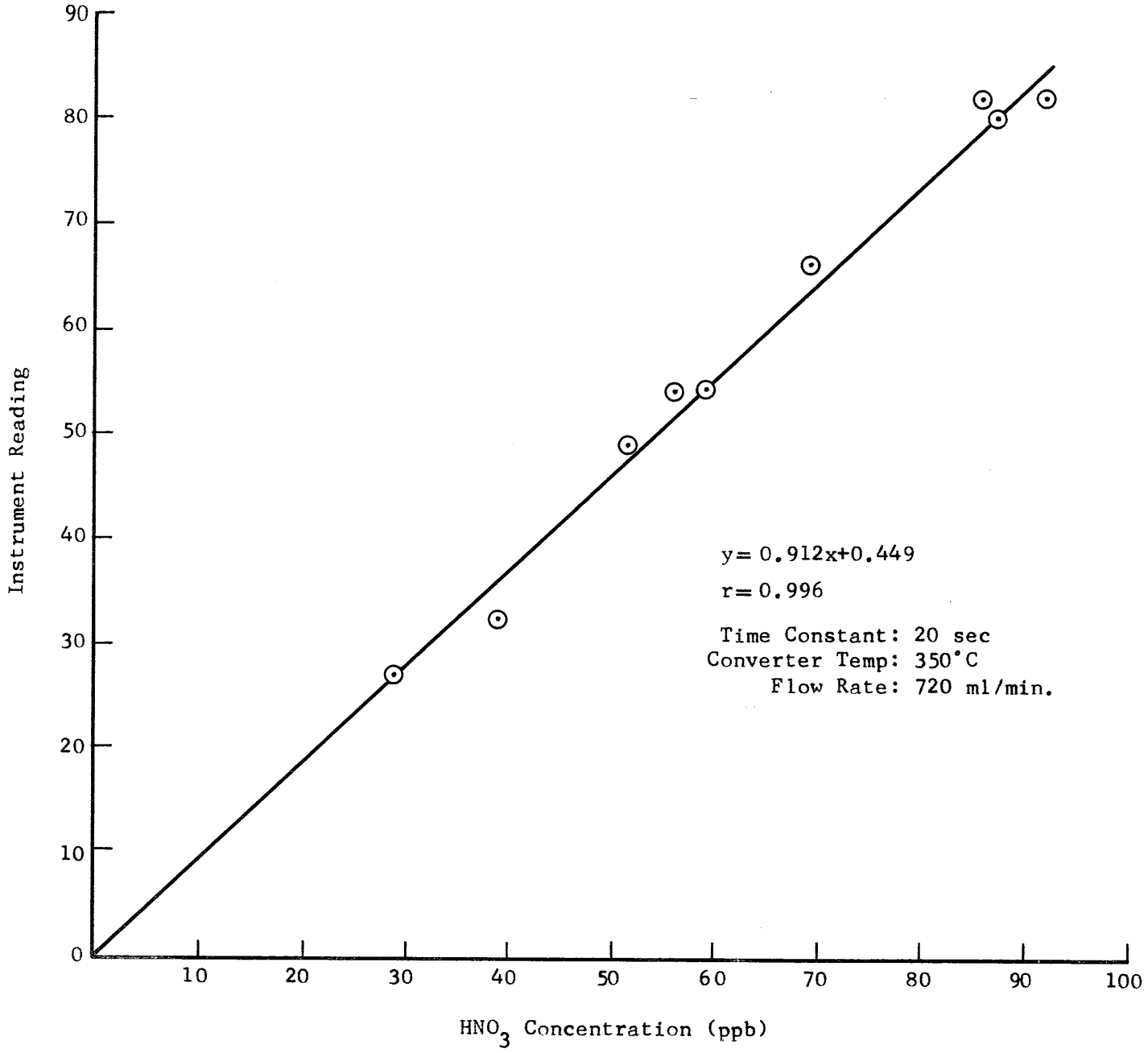


Figure 6
MONITOR LABS RESPONSE TO HNO_3 ON 100ppb RANGE



assess the effect of particulate matter on the observed HNO_3 levels by the Okita procedure.

2. Results

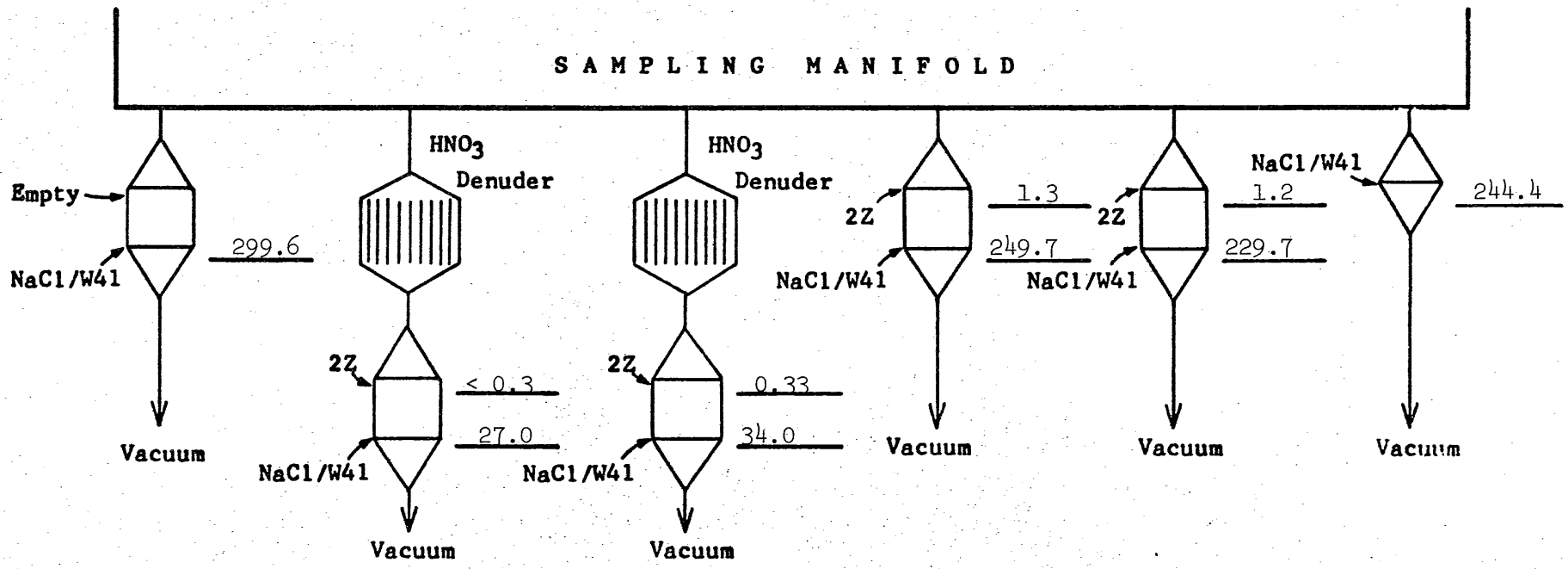
Figures 7 through 10 show schematically the design for the four experiments which yielded useful data, 16 C - F, together with individual filter results. Two denuder plus after-filter systems as well as two units for HNO_3 collection by the Okita method sampled in parallel. In addition, two NaCl/W41 samplers were operated without prefilters. One of the NaCl/W41 samplers had an empty holder (a stacked Nuclepore filter holder) in the prefilter position. Based on the experience gained in atmospheric sampling (Section V), no filter heating was employed. Experiments 16 C and E used clean prefilters while D and F used prefilters loaded with about 300 and 800 µg atmospheric particulate matter, respectively.* For trials D and F the reported nitrate values for the prefilters include atmospheric nitrate. The atmospheric nitrate values are expressed in units of µg/filter and $\mu g/m^3$ based on the volume of air sampled in the subsequent laboratory exposure.

Nitric acid values obtained by the three techniques are shown in Table 13. Results discussed in Section III C indicate that the diffusion denuder was about 88% efficient for HNO_3 removal. The method of HNO_3 generation as well as the absence of significant NO_3^- levels on clean Teflon prefilters suggest that the 12% average NO_3^- penetration through the denuder was indeed HNO_3 and not particulate nitrate. Accordingly, particulate nitrate and "HNO_3 by difference" values are shown calculated with apparent particulate nitrate (PN) values (i.e., equating all nitrate penetrating the denuder with particulate nitrate) and with results corrected assuming PN = 0 except when atmospheric particulate-loaded Zefluor filters were employed. Apparent "HNO_3 by difference", while generally lower than HNO_3 by the Okita method, agrees relatively well with HNO_3 by the Monitors Labs chemiluminescent analyzer. However, our experience suggests the Monitor Labs unit tends to give low results in laboratory trials because of HNO_3 losses to tubing walls in excess of those experienced by the other techniques. Corrected "HNO_3 by difference" agrees well with HNO_3 by the Okita method. Significant difference occurs only when the prefilter is relatively heavily loaded with atmospheric particulate matter. The ratios of means, relative to the corrected HNO_3 by difference, show agreement by the three techniques within 11%. Relative to uncorrected HNO_3 by difference, results agree, on average, within 17%. In trial 16F with 768 µg TSP per prefilter, the Okita method is 13 to 18% lower than the other techniques reflecting the retention of HNO_3 on the prefilter.

Future atmospheric trials sampling nitric acid by the difference method will employ a denuder with sufficient total MgO tube length to insure > 99% HNO_3 removal. Under these conditions the present

* Samples for each trial collected simultaneously in Berkeley.

Figure 7 SCHEMATIC COMPILATION OF HNO_3 FILTER COLLECTION RESULTS, TRIAL 16C ($\mu g/m^3$)



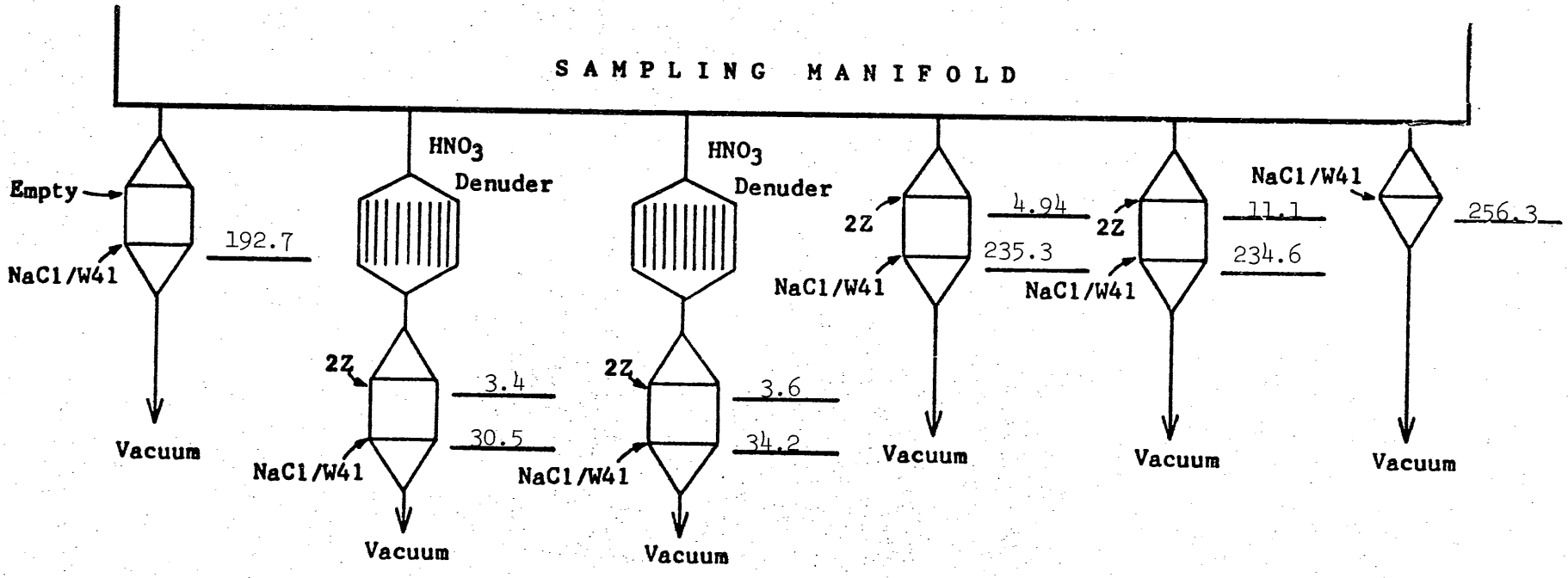
Experimental Conditions:

R.H.(%)	30
Temp., °C	32
Prefilter Atm. Partic. Loading	none
Sampling Time, hrs. (flow rate)	4.0 (20 Lpm)

Abbreviations: 2Z = 2μm pore size Zefluor filter

NaCl/W41 = NaCl-impregnated Whatman 41 filter

Figure 8 SCHEMATIC COMPILATION OF HNO_3 FILTER COLLECTION RESULTS, TRIAL 16D ($\mu g/m^3$)



Experimental Conditions:

R.H.(%) 30

Temp.,°C 32

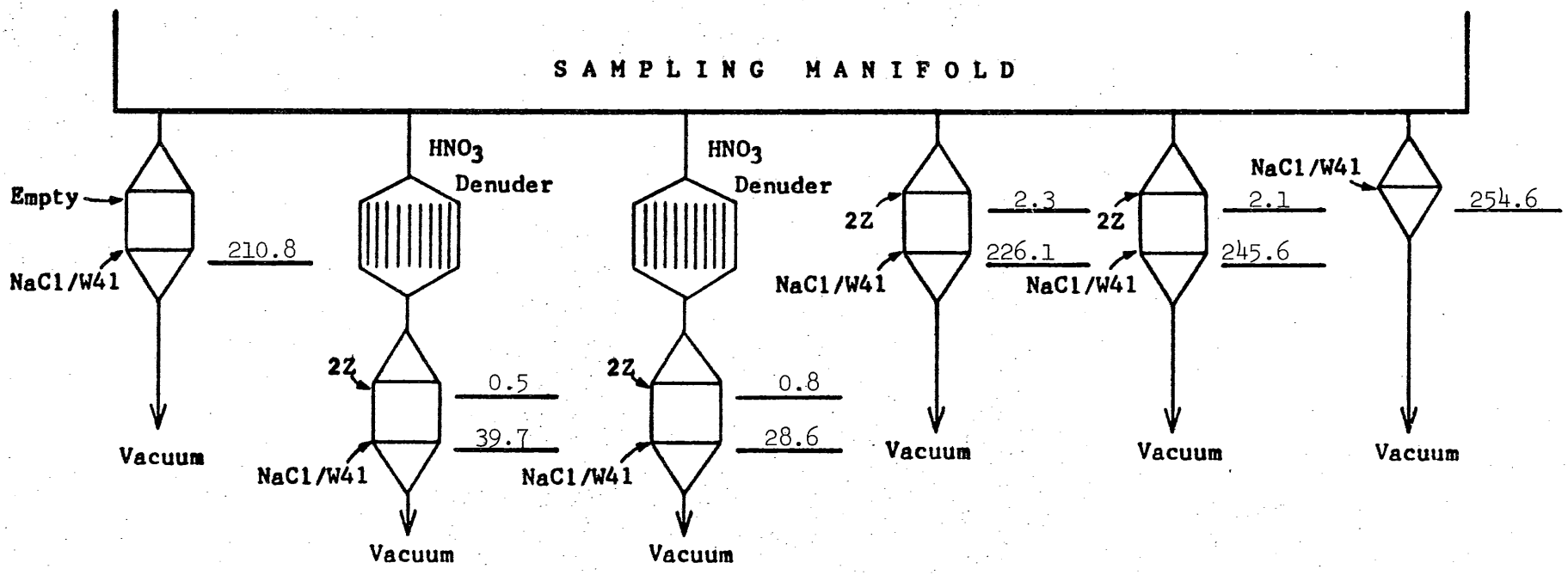
Prefilter Atm. Partic. Loading 271 ± 87 µg (Atm. Partic. contributes 1.0 $\mu g/m^3$ to observed values on 2Z filters)

Sampling Time, hrs. (flow rate) 4.5 (20 Lpm)

Abbreviations: 2Z = 2µm pore size Zefluor filter

NaCl/W41 = NaCl-impregnated Whatman 41 filter

Figure 9 SCHEMATIC COMPILATION OF HNO_3 FILTER COLLECTION RESULTS, TRIAL 16E ($\mu g/m^3$)



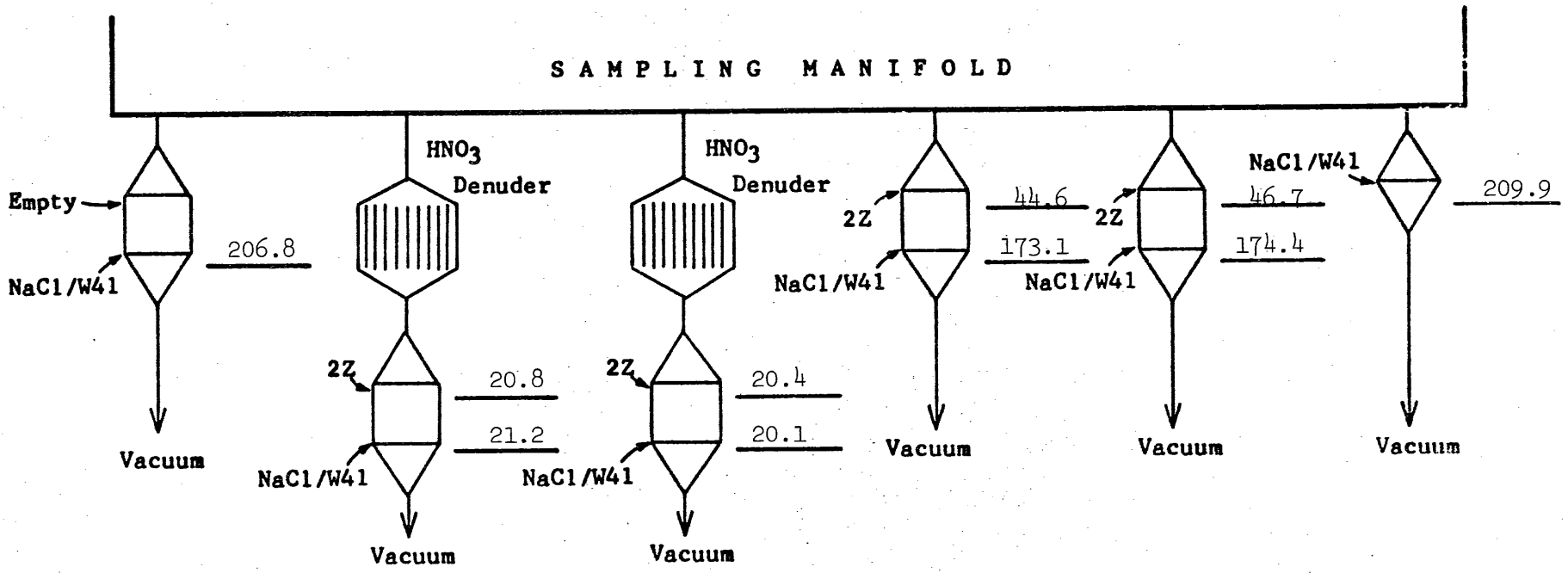
Experimental Conditions:

R.H.(%)	50
Temp.,°C	21
Prefilter Atm. Partic. Loading	none
Sampling Time, hrs. (flow rate)	4.0 (20 Lpm)

Abbreviations: 2Z = 2μm pore size Zefluor filter

NaCl/W41 = NaCl-impregnated Whatman 41 filter

Figure 10 SCHEMATIC COMPILATION OF HNO_3 FILTER COLLECTION RESULTS, TRIAL 16F ($\mu g/m^3$)



Experimental Conditions:

R.H.(%)	50
Temp.,°C	21
Prefilter Atm. Partic. Loading	768 ± 5 µg (Atm. Partic. contributes 6.1 $\mu g/m^3$ to observed values on 2Z filters)
Sampling Time, hrs. (flow rate)	4.0 (20 Lpm)

Abbreviations: 2Z = 2µm pore size Zefluor filter

NaCl/W41 = NaCl-impregnated Whatman 41 filter

Table 13 INTERMETHOD COMPARISON OF HNO_3 SAMPLING TECHNIQUES UNDER LABORATORY CONDITIONS ($\mu g/m^3$)

Trial	Temp. °C	R.H. (%)	Prefilter Loading, µg	TIN[a]	PN		HNO_3 by Difference[c]		HNO_3 by Okita Method[d]	HNO_3 by Monitor Labs Analyzer[e]
					Apparent[b]	Corrected[f]	Apparent	Corrected[f]		
16C	32	30	none	241 ± 14	30.5 ± 4.9	0	211 ± 16	241 ± 14	239 ± 14	215 ± 11
16D	32	30	271 ± 87	243 ± 4	35.9 ± 2.8	1.0	207 ± 5	242 ± 87	235 ± 0.5	212 ± 9
16E	21	50	none	238 ± 14	34.8 ± 7.6	0	203 ± 16	238 ± 14	236 ± 14	206 ± 4
16F	21	50	768 ± 5	219 ± 2.4	41.3 ± 1.1	6.1	178 ± 3	213 ± 2.4	174 ± 1	201 ± 7
					Ratio of Means:		0.85	1.0	0.95	0.89
							1.0	1.17	1.11	1.04

a. Total inorganic nitrate.

b. The apparent particulate nitrate assuming all nitrate penetrating the denuder to be particulate nitrate (see Table and text).

c. TIN less PN.

d. The nitrate on NaCl/W41 filters downstream of Teflon prefilter.

e. Continuous readings averaged over the four-hour sampling time.

f. Correction assumed nitrate penetrating denuder was HNO_3. Thus corrected values are either zero or the nitrate contributed by the atmospheric particles on the Teflon filter.

method comparison employing the "corrected" results should be more relevant.

Since the atmospheric particulate matter contains nitrate (in Trial 16F it corresponded to about 6 $\mu g/m^3$), in principle the HNO_3 results might err in either direction depending on the dominance of HNO_3 adsorption on the prefilter or NH_4NO_3 dissociation. In the present laboratory trial which maintained HNO_3 constant at about 80 ppb, such dissociation should be repressed, favoring the observed negative deviations in HNO_3 (and increase in nitrate retained on the prefilter used to measure particulate nitrate by the Okita method). However, as suggested above, such retention of HNO_3 may not be observable in atmospheric sampling (where HNO_3 levels can drop to low levels) especially under conditions of high particulate nitrates.

In addition to trials 16 C - F, two similar experiments were attempted at 80% R.H. and 16°C. The conditions approach those experienced at night and early morning in atmospheric sampling, for which R.H. values > 90% were often found. However, under these conditions losses of about 99% of the HNO_3 (at a calculated 80 ppb) was experienced ahead of the filter samplers apparently by collection on the walls of the glass dilution system and sampling manifold. The effective scavenging of HNO_3 by surfaces under these conditions suggests that retention of atmospheric HNO_3 on particulate matter-loaded Teflon prefilters (and perhaps on suspended particles) at high R.H. should be efficient as well. Conversely, loss of NH_4NO_3 by dissociation to HNO_3 should be repressed.

IV. LABORATORY EVALUATION OF SAMPLING TECHNIQUES FOR H_2SO_4

A. Introduction

Previous atmospheric sampling trials in Pittsburg[1] as well as those for the present study in the Los Angeles Basin included both respirable particulate hi-vol and lo-vol sampling for H_2SO_4. The latter used a denuder for removal of atmospheric NH_3 in an attempt to increase the stability of any acidic aerosol collected. However, the use of an ammonia denuder introduces a potentially significant source of error in monitoring the acidity of atmospheric particulates. The system H_2O-NO_3^--$SO_4^=$-NH_4^+-HCO_3^--H_2CO_3 such as might be found in a given aerosol particle, may exist in equilibrium with corresponding materials in gas phase (e.g., HNO_3, NH_3, CO_2). The removal of NH_3 from the air stream might, therefore, induce increased acidity in the particulate by causing dissociation of NH_4^+ to gaseous NH_3 and H^+. The latter might then react preferentially with the most alkaline material remaining, e.g., HCO_3^-, forming the weak acid H_2CO_3, not measurable as strong acid by the titrimetric method used. However, if the bicarbonate anion is consumed, further NH_3 loss could lead to either H_3O^+ or HSO_4^-. In either case, increased strong acid levels would then be observed. Brosset has predicted that, at least for aerosols which resemble aqueous solutions, such NH_3 loss should occur.[20] In addition to NH_3 loss, transfer of phosphorous acid from the tubes of the denuder to the filters would also cause increase in the measured strong acid.

B. Experimental Procedure

To assess these possible sources of artifact strong acid, Teflon filters were loaded with $\leq$ 0.2 μm $(NH_4)_2SO_4$ particles or $(NH_4)_2SO_4$-NH_4NO_3 aerosol mixtures prepared from a solution of the two salts. The loaded filters were exposed to air purified by removal of NO_x, ozone and organics heavier than ethane using triethanolamine and charcoal. The purification train is described elsewhere.[35] Atmospheric CO_2 was not significantly removed and CO_2 levels of $\geq$ 400 ppm were expected. Transfer of phosphorous acid to the filter was measured by sampling humidified air through the denuder followed by a clean Teflon filter. Strong acid was measured as previously described.[1]

C. Results

Table 14 summarizes the experiments performed running two filters in duplicate. Acidity levels were compared to those of filters loaded

Table 14

Assessment of Artifact H^+ Formation Caused by Use of An Ammonia Denuder at 20°C[a]

Particulate Loading	Clean Air Sampling Conditions	Observed H^+ Increase (as µg H_2SO_4 per filter)
None	28 Lpm, 6 hours 80% R.H.	Not detected[b]
400 µg 0.2 ± 0.1 µm $(NH_4)_2SO_4$[c]	28 Lpm, 6 hours 50% R.H.	Not detected[b]
416 µg 0.2 ± 0.1 µm $(NH_4)_2SO_4$	28 Lpm, 6 hours 90% R.H.	Not detected[b]
370 µg 0.2 ± 0.1 µm 11:1 w/w $(NH_4)_2SO_4$:NH_4NO_3[c]	28 Lpm, 6 hours 58% R.H.	Not detected[b]
80 µg 0.2 ± 0.1 µm 0.35 w/w $(NH_4)_2SO_4$:NH_4NO_3[c]	28 Lpm, 6 hours 58% R.H.	Not detected[b]

a. All results based on filters run in duplicate side-by-side.

b. Filter acidity unchanged from that of filters not exposed to clean air.

c. Loading estimated from loading rate in other trials.

with equal amounts of the salts but not exposed to the air stream. At 90% R.H., $(NH_4)_2SO_4$ and the $(NH_4)_2SO_4$-NH_4NO_3 mixtures should exist as concentrated solutions (with dissolved CO_2)* in droplets on the filter, conditions which should favor NH_3 loss as the system strives to establish gas-liquid equilibrium. Nevertheless, no measurable acidity increase was observed. Similarly, no increase in acidity was observed with the blank Teflon filter.

In principle, NH_3 could be formed from dissociation of NH_4^+-containing particles during the 0.2 second calculated residence time within the NH_3-denuder tubes. However experiments with NH_4NO_3, described in Section III, did not support the significance of such dissociation making loss of NH_3 from sulfate salts improbable, as well.

We conclude, therefore, that the use of the NH_3 denuder does not cause artifact H^+ formation either from NH_3 loss from salts on the filter, or by transfer of phosphorous acid.

---

* The equilibrium concentration of H_2CO_3 in water droplets in contact with air is about 10^{-5}M.[21]

V. ATMOSPHERIC SAMPLING

A. Sampling Strategy

Sampling was performed during July, 1979 for eight days at each of two sites, Lennox and Claremont, California. The sampling strategy is outlined in Table 15. Lennox is in proximity to numerous sulfur oxide emission sites, and might, therefore, be subject to relatively high concentrations of H_2SO_4 (Figure 11). Claremont is about 50 km east of downtown Los Angeles, relatively distant from strong SO_x emission sources. It was expected to exhibit low acidic sulfate levels but elevated levels of nitric acid and particulate nitrate.

B. Experimental Procedures

The analytical methods used and their precision, accuracy and limits of detection are shown in Table 16. In general, procedures followed were those described for the preliminary field study in Pittsburg, California.[1,23] However techniques were modified to improve the recovery of H_2SO_4. It was postulated that some of the loss of H_2SO_4 previously observed resulted from neutralization by ammonia liberated by dissociation of NH_4NO_3 or other NH_3-containing materials on the filter. To minimize such effects, samples were dried in vacuum to remove weakly bound NH_3, and stored at low temperature. In addition, four-times larger filter sections were extracted to decrease the limit of detection for H_2SO_4. Details are as follows.

Immediately following sampling, the samples for H_2SO_4 and H^+ analysis were stored at $\leq$ -20°C. Samples were held at room temperature for 30 min drying at $\leq$ 1 mm Hg, during sectioning in an NH_3-free chamber under dry N_2, and just prior to benzaldehyde addition. With hi-vol samples, 70 cm^2 filter sections were extracted in 15 mL benzaldehyde. After 15 min centrifugation at 2000 to 2500 rpm, 10 mL of the extract were recovered from the clear supernatant. Sulfate was transferred by liquid-liquid extraction into 3 mL H_2O which was analyzed for H_2SO_4 by the AIHL microsulfate method.[26] With lo-vol samples the 47 mm Teflon filter was sectioned in quarters, two quarters being extracted in 10 mL benzaldehyde. Nine mL of the extract were recovered for analysis of H_2SO_4 as $SO_4^=$ following re-extraction into H_2O. The remaining two quarters were extracted in 10 mL water for H^+ and $SO_4^=$ analysis. Both benzaldehyde and aqueous extractions employed 60 min mechanical shaking with an Eberbach Model 6000 platform shaker. Atmospheric ammonia was sampled on oxalic acid-impregnated Gelman AE filters at 25 Lpm with an unheated sampler.[1] A Gelman type A glass fiber (pH = 7.6) filter removed particulate matter. NH_3 was determined as NH_4^+ using an Orion ion-specific electrode.

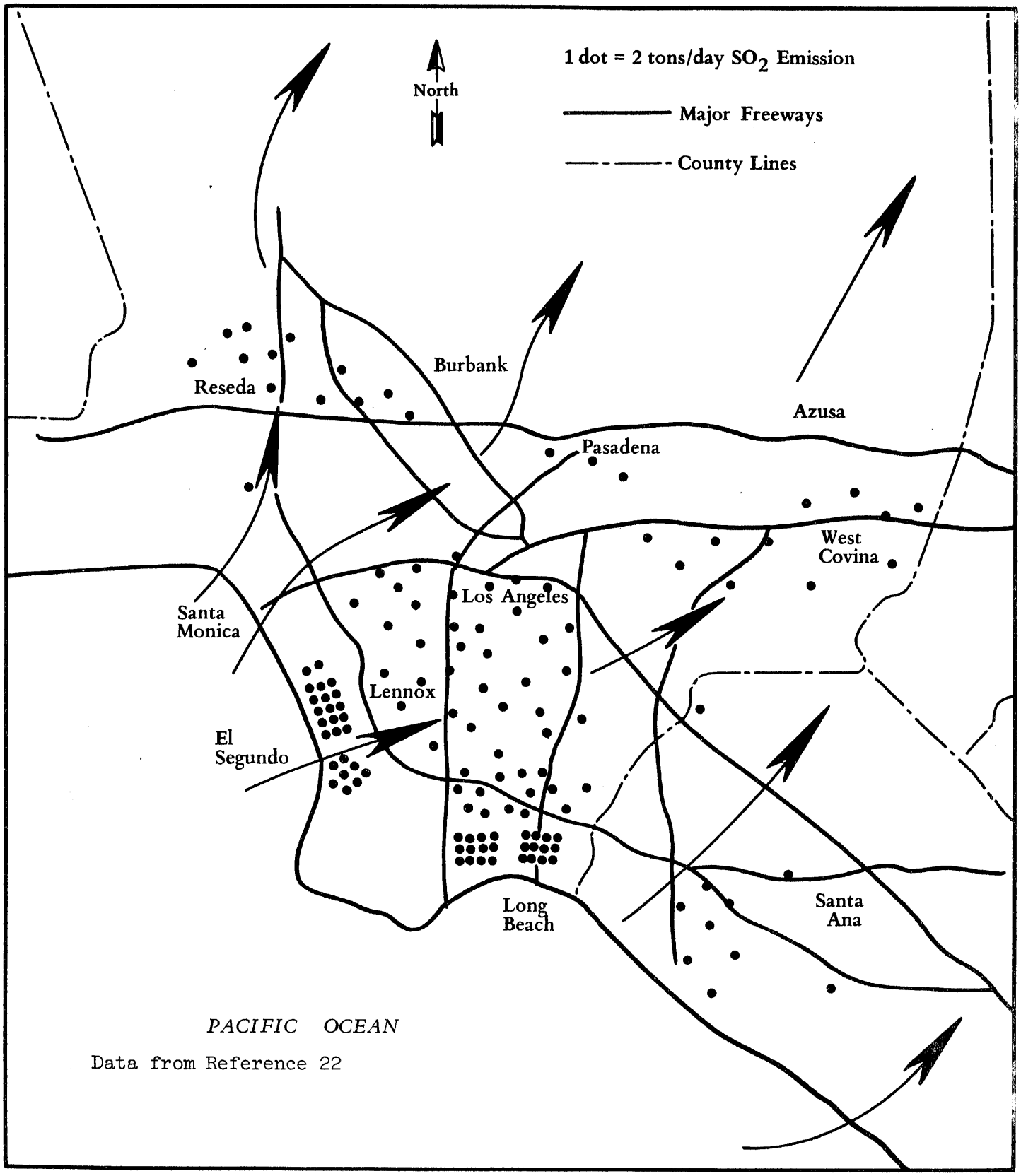
Table 15

Sampling Strategy at Lennox and Claremont, CA

Sampler	Flow Rate, m^3/min	Filter	Filter Change Frequency, hrs	Species Measured
Respirable (< 3.5 μm) particulate hi-vol	1.1	Acid-washed Pallflex 2500 QAO quartz fiber	2 to 8	H_2SO_4, H^+, $SO_4^=$, NO_3^-, NH_4^+
Respirable (< 2.5 μm) particulate lo-vol with NH_3 denuder	0.028	Zefluor (Teflon), 2 μm pore size[a]	8	H_2SO_4, H^+, $SO_4^=$
Total nitrate sampler	0.020	Zefluor plus NaCl/W41[b] or Ghia nylon	2 to 8	NO_3^-
Total particulate NO_3^- sampler using acid gas denuder	0.020	Zefluor plus NaCl/W41 or Ghia nylon	2 to 8	NO_3^-
Ammonia	0.025	Gelman A glass fiber prefilter plus oxalic acid/Gelman AE	2 to 8	NH_3 as NH_4^+, NO_3^- on glass fiber prefilter
Bendix Model 8002 O_3 analyzer		---	continuous	O_3
Meloy Model 5A160-2 total sulfur analyzer		---	continuous	SO_2 plus H_2S
Teco Model 14 NO-NO_2 analyzer		---	continuous	NO, NO_2

a. Ghia Corp., Pleasanton, CA.

b. NaCl-impregnated Whatman 41 (cellulose) filter.



Data from Reference 22

SO_2 EMISSIONS AND PREVAILING WIND PATTERNS
Figure 11

Table 16

Summary of Analytical Methods and their Precision, Accuracy and Limits of Detection

Species Analyzed	Method	Reference	Precision (C.V.), %	Limit of Detection, $\mu g/m^3$	Analytical Accuracy, %
H_2SO_4 (Hi-vol)	Benzaldehyde Extraction-AIHL $SO_4^=$ analysis	24, 1, 23	13% at < 1 $\mu g/m^3$[a] > 1 $\mu g/m^3$, see text	--[d]	Not determined[g]
H_2SO_4 (Lo-vol)	Same as above	24, 1, 23	Not determined	--[d]	Not determined[g]
H^+ (Hi-vol) as H_2SO_4	Titration to pH = 4.0	25, 1, 23	3.6% at > 1.0 $\mu g/m^3$[a] 40% at 0.5 $\mu g/m^3$	0.5[c]	Not determined[g]
H^+ (Lo-vol) as H_2SO_4	Same as above	10, 1, 23	Not determined	Est. 0.3	Not determined[g]
NH_4^+ (Hi-vol)	Selective ion electrode		Mean 13% for 0.4 to 6 $\mu g/m^3$ samples[a]	0.2[c]	119 at 0.6 $\mu g/m^3$[c]
$SO_4^=$ (Hi-vol)	AIHL micro $SO_4^=$ [k]	26	5.8[b]	0.1[c]	106[h]
$SO_4^=$ (Lo-vol)	AIHL micro $SO_4^=$ [k]	26	4.0[b]	0.2	102[i]
NO_3^- (Hi-vol)	Automated Cu-Cd reduction-diazotization	27	3.3[a]	0.7[c]	98
NO_3^- (Lo-vol)	Same as above	27	6.0	1.1[c]	98
NO_3^- (NH_3 sampler prefilter)	Gelman A glass fiber (pH = 7.6)[e]		0.9[b]	1.1[c]	98
NH_3 as NH_4^+	Oxalic acid on Gelman AE. Selective ion electrode.	28, 1	Not determined	0.8[c]	119 at 0.6 $\mu g/m^3$[j]
HNO_3 (nylon filter)	Particulate removal with Teflon prefilter[e]	3, 1	7[f]	1.1[c,d]	See text
HNO_3 (NaCl/W41)	Same as above	2, 1	7[f]	1.1[c,d]	See text
HNO_3 (by difference)	See text	16	See text	Not determined	See text

a. Based on analysis of separate filter sections removed and extracted at about the same time.

b. Based on re-analysis of the same filter extracts on a different day.

c. Calculated for 4-hour samples.

d. Subject to positive interference making limit of detection uncertain.

e. Quantitation by the automated Cu-Cd reduction, diazotization method.

f. From laboratory studies in Section III.

g. Recovery studies are described in References 1 and 23.

h. Compared to the mean of analysis of 24 Hi-vol filter extracts by six methods.

i. Compared to the Dionex ion chromatograph for analysis of 24 Lo-vol samples.

j. Based on recovery with standards. Comparison with simultaneous atmospheric NH_3 measurements by Fourier transform infrared spectroscopy (FTIR) for 7, 2 or 4-hour periods consistently 2.5 ± 0.5 $\mu g/m^3$ lower NH_3 by the filter technique with atmospheric levels of 4.1 to 7.8 $\mu g/m^3$.

k. Samples were pre-treated with Bio-Rad AG 30W-X8 cation exchange resin to remove cationic interferents.

The precision of H_2SO_4 determinations by benzaldehyde extraction, as measured by duplicate filter sections removed from the same filters, decreased sharply with increasing H_2SO_4 level. Above 1 $\mu g/m^3$ the mean C.V. was 85% (n = 3) compared to 13% at < 1 $\mu g/m^3$ (n = 9). Filter sections removed after an additional one-month storage (at -10°C) averaged 6% of the initial H_2SO_4 determination. These results reflect, most probably, the extreme sensitivity of H_2SO_4 recovery to details in sample handling (e.g., the cumulative exposure to NH_3). The atmospheric H_2SO_4 values are, in general, considered minimum values.

Nitric acid was sampled with 47 mm, NaCl-impregnated Whatman 41 (NaCl/W41) cellulose filters and with Duralon (Millipore Corp.) or Ghia Corp. nylon filters. For a number of sampling periods both NaCl/W41 and nylon filters were run in parallel. Teflon prefilters were used to remove particulate matter. Nitric acid values obtained in this way will be referred to as "HNO_3 by filter collection". Prefilters and HNO_3 collection filters were mounted in series in Nuclepore multiple filter holders with 3.2 cm I.D. 15 cm length polycarbonate inlet tubes. The sum of the nitrate on the Teflon prefilter and nitric acid (as NO_3^-) on the nylon or NaCl/W41 after-filter equalled the total inorganic nitrate (TIN). The efficiency of the prefilters for collection of particulate matter is > 99.9% as measured with room air dust and a condensation nuclei counter.[29] In some cases following each sampling period, ambient air, heated to a temperature which produced a relative humidity of < 15% (about 50°C), was sampled for three minutes at 20 Lpm to desorb nitric acid possibly retained on the prefilter and/or walls of the sampler. In parallel with the Teflon prefilters, particulate nitrate (PN) was sampled following passage of the atmospheric sample through an inlet tube as described above and an acid gas denuder discussed in Section III C. Assuming no loss of particulate nitrate in the denuder, the TIN less PN should equal the gaseous nitrate (i.e., HNO_3). This is here referred to as "HNO_3 by difference". Nitrate was extracted from filters with 10 mL distilled H_2O or, for nylon filter, 5 mL 0.1N NaOH, by 60 min agitation using an Eberbach Model 6000 shaker. Basic extracts were neutralized with 5 mL 0.1N HCl prior to NO_3^- determination.

C. Summary of Data

Results obtained with the hi-vol and lo-vol samplers and the nitrate reference sampler are tabulated in Tables 17 through 22, in $\mu g/m^3$. The results are discussed in the following sections. To aid in data comparisons, graphical presentations are presented in nano-equivalents per m^3.

D. Particulate Acid Results

1. Lennox

The results for H_2SO_4, H^+, NH_4^+ and NH_3 are shown in Figure 12. In addition, wind speed and direction are indicated by arrows,

Table 17

Analysis of Respirable Particulate Hi-Vol and NH_3 Sampler Results from Lennox, CA ($\mu g/m^3$)

Date	Time (PDT)	Hi-Vol Sampler[a] H_2SO_4	H^+	NH_4^+	$SO_4^=$	NO_3^-	NH_3 Sampler[b] Prefilter NO_3^-	NH_3 as NH_4^+
7/10/79	6-8	0.2	0.6	< 0.7	3.5	< 1.5	6.6	3.8
	8-10	0.1	< 0.2	< 0.7	3.7	2.0	18.4	3.5
	10-14	0.2	0.3	0.3	5.3	2.6	28.9	0.9
	14-18	0.1	< 0.1	0.7	6.1	0.9	48.1	1.2
	18-22	0.1	< 0.1	< 0.3	3.6	< 0.7	9.8	1.2
	22-06	0.0	0.2	< 0.2	1.3	0.5	2.4	1.7
7/11/79	6-8	0.1	< 0.2	< 0.7	2.5	< 1.7	4.1	1.9
	8-10	0.1	< 0.2	< 0.7	5.6	1.4	8.7	3.0
	10-14	0.1	0.5	< 0.3	3.8	2.1	15.9	3.1
	14-18	0.1	0.5	1.4	8.2	1.8	31.5	1.2
	18-22	0.1	1.1	1.2	7.5	2.2	32.2	< 0.9
	22-06	0.1	< 0.06	2.0	5.1	2.8	17.3	2.1
7/12/79	6-8	0.2	< 0.2	1.6	7.3	2.7	13.2	1.9
	8-10	0.3	< 0.2	1.5	10.1	3.2	17.3	2.4
	10-14	0.1	< 0.1	1.3	7.6	2.3	17.4	4.1
	14-18	0.1	< 0.1	1.1	8.8	1.4	25.5	2.4
	18-22	0.1	< 0.1	0.4	4.7	1.7	10.4	3.4
	22-06	0.1	0.7	2.2	8.9	1.2	13.3	1.0
7/13/79	6-8	0.3	1.6	< 0.7	11.3	< 1.5	14.4	< 1.9
	8-10	0.3	2.4	< 0.7	10.9	< 1.4	17.3	< 1.9
	10-14	0.3	2.4	2.0	13.2	< 0.7	15.9	< 0.9
	14-18	0.3	1.1	2.4	11.8	< 0.7	14.3	0.9
	18-22	0.1	0.3	0.5	6.0	< 0.7	5.3	0.8
	22-06	0.1	0.8	3.0	9.2	< 0.5	16.0	0.6
7/14/79	6-8	0.3	2.1	0.3	13.1	< 1.5	< 2.1	< 1.9
	8-10	0.3	1.6	1.3	12.8	< 1.4	29.2	< 1.9
	10-14	0.3	3.2	1.4	14.1	0.8	25.8	< 0.9
	14-18	0.1	0.2	0.7	6.2	< 0.7	14.7	< 0.9
	18-22	0.1	< 0.1	< 0.3	3.1	< 0.7	4.1	1.5
	22-06	0.1	1.3	0.4	4.7	0.4	6.3	0.5
7/15/79	6-8	7.6	7.5	0.7	10.7	< 1.5	15.8	< 1.9
	8-10	1.1	5.8	2.1	14.8	< 1.5	16.9	< 1.9
	10-14	0.3	4.3	2.1	12.3	< 0.7	22.6	< 1.0
	14-18	0.2	2.0	1.3	8.3	< 0.7	7.6	< 0.9
	18-22	0.3	0.5	0.9	4.5	< 0.7	4.0	< 0.9
	22-06	1.5	2.2	1.3	8.1	< 0.4	8.6	0.7
7/16/79	6-8	0.4	4.4	4.4	20.3	< 1.3	25.3	< 1.7
	8-10	2.0	9.3	1.5	15.2	< 1.7	23.4	< 2.1
	10-14	10.9	4.9	0.7	10.2	< 0.7	16.7	< 0.9
	14-18	0.4	1.5	0.4	5.8	< 0.7	8.1	< 0.9
	18-22	0.1	0.3	1.0	4.8	0.9	6.7	1.3
	22-06	0.2	--[c]	--[c]	5.7	1.7	12.1	1.7
7/17/79	6-8	0.2	< 0.2	4.1	8.3	3.9	16.0	4.0
	8-10	0.2	0.5	3.7	7.1	5.3	20.3	3.5
	10-14	0.2	0.9	1.7	7.5	1.0	22.4	2.5
	14-18	9.6	1.1	2.0	10.7	1.0	45.0	< 1.0
	18-22	0.0	0.5	1.1	4.5	1.2	8.5	2.0
	22-06	4.3	1.0	1.6	6.7	1.0	6.3	1.9

a. Collected on acid-washed Pallflex quartz 2500 QAO filters.

b. Samples collected on oxalic acid impregnated Gelman AE glass fiber filters following particle removal with Gelman A glass fiber prefilters.

c. Sample lost.

Table 18

Analysis of Respirable Particulate Hi-Vol and NH_3 Sampler Results from Claremont, CA ($\mu g/m^3$)

		Hi-Vol Sampler[a]					NH_3 Sampler[b]	
Date	Time (PDT)	H_2SO_4	H^+	NH_4^+	$SO_4^=$	NO_3^-	Prefilter NO_3^-	NH_3 as NH_4^+
7/22/79	6-8	0.3	< 0.2	< 0.7	1.4	< 1.5	16.2	4.3
	8-10	0.1	< 0.2	1.6	4.9	6.6	31.0	6.8
	10-14	0.1	1.5	1.9	7.6	1.6	46.0	3.1
	14-18	0.1	0.5	1.4	6.9	1.0	41.6	1.5
	18-22	0.2	< 0.1	1.0	5.6	1.4	18.5	2.1
	22-06	0.7	0.1	1.4	4.5	1.5	16.2	2.5
7/23/79	6-8	0.3	< 0.2	2.5	5.8	5.7	30.2	5.0
	8-10	0.2	< 0.2	6.2	7.3	12.0	55.9	< 1.5
	10-14	0.3	0.3	2.1	7.4	2.6	69.0	3.8
	14-18	1.7	1.2	4.6	12.4	2.2	70.2	0.6
	18-22	3.2	0.4	3.5	9.9	2.6	41.5	0.8
	22-06	0.9	< 0.06	2.7	6.2	2.8	16.2	2.8
7/24/79	6-8	1.9	< 0.2	2.6	7.0	8.1	21.3	7.1[c]
	8-10	1.5	< 0.2	9.6	11.1	28.2	62.1	---
	10-14	0.6	0.8	2.5	14.5	11.7	80.2	4.0
	14-18	1.6	1.0	0.9	12.5	1.6	65.1	0.8
	18-22	0.2	2.2	5.2	16.4	2.0	46.6	0.8
	22-06	0.1	0.3	7.7	12.8	6.5	22.2	3.4
7/25/79	6-8	4.5	0.5	4.1	9.2	8.1	23.2	4.6
	8-10	1.0	0.7	5.8	15.8	15.5	45.1	4.1
	10-14	0.1	0.7	6.4	14.6	< 0.7	73.0	1.4
	14-18	0.3	1.0	3.0	11.2	1.2	57.3	1.0
	18-22	0.1	< 0.1	---[c]	16.9	1.4	37.5	0.7
	22-06	0.1	0.1	4.7	8.4	6.2	18.4	4.1
7/26/79	6-8	0.2	< 0.2	8.4	14.3	16.5	36.5	9.8
	8-10	0.9	< 0.2	12.8	17.1	13.6	37.3	< 1.5
	10-14	0.7	0.8	10.9	18.5	11.4	82.0	1.5
	14-18	0.5	2.0	6.7	18.7	1.9	60.5	0.7
	18-22	1.5	0.6	3.1	10.0	3.0	36.3	< 0.8
	22-06	0.3	0.4	4.5	7.9	6.0	22.7	2.8
7/27/79	6-8	4.3	0.8	4.4	10.2	12.5	46.5	2.8
	8-10	0.5	1.0	10.8	12.6	27.7	78.2	4.9
	10-14	1.5	0.5	6.7	12.4	11.0	82.3	2.5
	14-18	0.7	1.3	4.3	16.2	1.9	57.8	< 0.8
	18-22	0.2	0.4	2.3	9.0	1.9	38.2	0.8
	22-06	0.1	0.4	2.9	6.1	4.0	89.6	5.4
7/28/79	6-8	0.2	1.6	2.1	6.0	4.5	31.1	< 1.5
	8-10	0.3	1.0	7.4	11.1	18.5	79.3	3.0
	10-14	0.4	0.9	5.6	9.6	7.9	82.3	2.3
	14-18	0.5	1.2	0.9	9.2	2.0	58.4	< 0.8
	18-22	0.2	0.5	2.7	8.8	2.5	41.3	< 0.8
	22-06	0.1	< 0.06	1.9	5.2	1.5	16.7	1.4
7/29/79	6-8	0.2	< 0.2	4.6	9.1	12.1	25.8	5.7
	8-10	0.3	< 0.2	6.5	12.7	19.9	74.6	7.8
	10-14	0.3	0.9	2.8	9.2	3.9	71.2	2.7
	14-18	0.5	0.8	3.4	15.2	1.4	56.3	1.2
	18-22	0.3[c]	1.3	6.2	17.5	3.8	46.6	< 0.8
	22-06	---[c]	0.4	5.6	12.8	6.2	27.3	1.7

a. Samples collected on acid-washed Pallflex quartz 2500 QAO filters.

b. See footnote b, Table 7.

c. Sample lost.

Table 19

Analysis of Lo-Vol Respirable Particulate Samples (with NH_3 Denuder) from Lennox, CA ($\mu g/m^3$)[a]

Date	Time (PDT)	H_2SO_4	H^+	$SO_4^=$
7/10/79	6-14	0.8	< 0.3	9.1
	14-22	2.1	< 0.3	14.5
	22-06	0.2	< 0.3	1.9
7/11/79	6-14	0.5	< 0.3	5.8
	14-22	1.7	0.3	10.7
	22-06	1.8	0.3	---[b]
7/12/79	6-14	0.6	0.6	12.9
	14-22	0.4	0.6	10.3
	22-06	0.6	0.7	17.4
7/13/79	6-14	0.5	4.5	17.9
	14-22	1.5	1.5	14.6
	22-06	0.4	1.9	14.8
7/14/79	6-14	1.3	4.6	21.2
	14-22	0.6	1.3	6.4
	22-06	0.6	2.6	8.4
7/15/79	6-14	2.4	8.6	17.4
	14-22	0.8	1.8	7.4
	22-06	0.6	1.9	14.5
7/16/79	6-14	1.7	8.4	21.1
	14-22	0.4	< 0.3	8.8
	22-06	0.3	< 0.3	7.5
7/17/79	6-14	0.4	< 0.3	9.4
	14-22	0.2	< 0.3	8.9
	22-06	0	10.6	12.0

a. Samples collected on 2.0 μm Teflon (Zefluor) filters.

b. Samples lost.

Table 20

Analysis of Lo-Vol Respirable Particulate Samples (with NH_3 Denuder) from Claremont, CA ($\mu g/m^3$)[a]

Date	Time (PDT)	H_2SO_4	H^+	$SO_4^=$
	6-14	0.4	< 0.3	10.3
7/22/79	14-22	0.4	< 0.3	8.7
	22-06	0.3	1.2	6.7
	6-14	1.0	0.6	12.1
7/23/79	14-22	1.2	1.2	19.0
	22-06	0.9	< 0.3	10.0
	6-14	1.0	2.3	20.2
7/24/79	14-22	0.7	3.1	22.4
	22-06	0.7	< 0.3	20.7
	6-14	0.4	< 0.3	22.2
7/25/79	14-22	0.4	0.6	20.9
	22-06	0.8	0.3	13.6
	6-14		Samples Lost	
7/26/79	14-22	1.0	0.9	21.0
	22-06	1.1	1.4	11.5
	6-14	1.0	2.0	16.9
7/27/79	14-22	1.3	1.5	20.1
	22-06	0.8	1.0	10.6
	6-14	0.8	0.8	14.7
7/28/79	14-22	2.5	0.6	14.5
	22-06	1.0	0.3	13.8
	6-14	0.6	1.3	17.5
7/29/79	14-22	0.9	< 0.3	22.1
	22-06	1.3	0.4	21.2

a. Samples collected on 2.0 μm pore size Teflon (Zefluor) filters.

Table 21

Nitrate and Nitric Acid Results with the Nitrate Reference Sampler at Lennox, CA ($\mu g/m^3$ as NO_3^-)

Date	Time (PDT)	Total Inorganic Nitrate Sampler			Particulate Nitrate Sampler			HNO_3 by Difference[c]
		Pre-filter	After-filter[b]	Total	Pre-filter	After-filter[b]	Total	
7/10/79	6-8	< 2.3	3.9	5.0	< 2.2	4.6	5.7	- 0.7
	8-14	10.9	21.4	32.3	5.9	8.9	14.8	17.5
	14-22	4.5	12.1	16.5	3.4	5.2	8.7	7.8
	22-06	1.6	1.2	2.8	< 0.5	1.1	1.4	1.5
7/11/79	6-14	4.5	3.4	7.9	3.1	2.4	5.4	2.4
	14-22	13.3	11.9	25.2	9.3	5.7	15.0	10.2
	22-06	7.8	6.2	14.1	6.6	6.2	12.8	1.2
7/12/79	6-14	9.2	6.0	15.2	4.4	4.8	9.2	6.0
	14-22	2.0	8.2	10.2	8.5	4.4	12.9	- 2.7
	22-06	5.9	4.8	10.6	4.9	2.9	7.8	2.8
7/13/79	6-14	5.7	7.6	13.3	5.3	3.9	9.2	4.1
	14-22	3.7	6.2	9.9	4.1	3.1	7.2	2.7
	22-06	5.7	7.5	13.2	6.9	3.7	10.6	2.6
7/14/79	6-14	4.9	18.8	23.7	3.2	6.1	9.3	14.4
	14-22	2.0	5.4	7.4	3.4	2.1	5.5	1.9
	22-06	2.8	3.6	6.5	2.3	1.5	3.8	2.7
7/15/79	6-14	3.5	15.1	18.5	2.9	4.5	7.4	11.1
	14-22	1.8	4.3	6.1	1.9	1.6	3.6	2.5
	22-06	2.0	6.3	8.3	2.1	3.3	5.4	2.9
7/16/79	6-14	1.4	18.4	19.8	1.0	6.3	7.3	12.5
	14-22	2.1	5.4	7.5	1.7	2.9	4.6	2.9
	22-06	4.7	5.3	9.9	3.0	5.0	8.0	2.0
7/17/79	6-14	6.2	11.5	17.7	4.7	7.3	12.1	5.6
	14-22	3.9	< 0.5	4.1	2.9	6.5	9.4	- 5.2
	22-06	3.4	3.3	6.6	1.7	3.5	5.2	1.5

a. All samples heated 3 min. at about 50°C following particulate collection.

b. Ghia nylon.

c. Total inorganic NO_3^- sampler minus particulate NO_3^- sampler results.

Table 22

Nitrate and Nitric Acid Results with the Nitrate Reference Sampler at Claremont, CA ($\mu g/m^3$ as NO_3^-)

Date	Time (PDT)	Total Inorganic Nitrate Sampler			Particulate Nitrate Sampler			HNO_3 by Difference[f]
		Pre-filter	After-filter	Total	Pre-filter	After-filter	Total	
7/22/79[a]	06-14	7.1	22.3[c]	29.4	4.1	14.1[c]	18.2	11.2
	14-22	4.6	19.5	24.1	2.7	6.3	9.1	15.0
	22-06	5.3	7.8	13.1	4.0	5.4	9.4	3.7
7/23/79[a]	0630-1030	13.2	34.4[d]	47.6	8.4	25.9[d]	34.3	13.3
	1030-1230	16.0	63.5	79.5	9.4	31.6	41.0	38.5
	1230-1430	14.1	67.1	81.2	6.5	20.9	27.4	53.8
	1430-1630	7.3	67.1	74.4	7.9	21.1	29.0	45.4
	1630-1830	7.7	78.6	86.3	5.6	19.0	24.6	61.7
	1830-2230	7.6	27.7	35.3	5.0	7.1	12.1	23.2
	2230-0630	9.6	4.5	14.1	6.9	1.9	8.8	5.3
7/24/79[b]	0630-1030	35.3	5.1[e]	40.4	3.1	4.5[e]	7.6	32.8
	1030-1230	33.9	34.9	68.8	21.4	27.3	48.7	20.1
	1230-1430	13.4	80.4	93.8	63.4	23.0	86.4	7.4
	1430-1630[g]	---	---	---	---	---	---	---
	1630-1830	8.1	45.4	53.5	6.4	12.1	21.4	35.0
	1830-2230	8.0	29.3	37.3	5.9	7.1	13.0	24.3
	2230-0630	18.4	4.4	22.8	17.0	2.4	19.4	3.4
7/25/79[b]	0630-1030	29.5	8.4[d]	37.9	22.0	12.5[d]	34.9	3.4
	1030-1230	26.8	48.7	75.5	13.2	14.8	28.0	47.5
	1230-1430	6.8	54.6	61.4	4.4	25.5	30.0	31.4
	1430-1630	6.8	57.1	64.9	3.8	20.9	24.7	39.2
	1630-1830	2.8	45.2	48.1	3.5	8.8	12.4	35.7
	1830-2230	8.9	19.9	28.8	6.3	6.4	12.7	16.1
	2230-0630	16.4	3.2	19.6	14.6	1.6	16.2	3.4
7/26/79[b]	0630-1030	57.2	7.5[c]	64.7	45.8	7.1[c]	53.0	11.7
	1030-1230	32.9	46.5	79.3	19.3	22.1	41.4	37.9
	1230-1430	11.3	80.4	91.7	< 2.1	< 2.1	< 4.2	89.6
	1430-1630	4.6	89.6	94.2	7.3	52.0	59.3	34.9
	1630-1830	5.1	62.5	67.6	3.4	15.0	18.4	49.2
	1830-2230	8.8	19.8	28.6	6.9	6.8	13.7	14.9
	2230-0630	17.6	5.3	22.9	15.4	2.8	18.2	4.7
7/27/79[a]	06-14	18.5	49.8[c]	68.2	11.8	36.7[c]	48.5	19.7
	14-22	4.2	25.4	29.5	3.4	10.4	13.8	15.7
	22-06	6.3	9.4	15.7	3.6	8.7	12.3	3.4
7/28/79[a]	06-14	22.6	41.5[c]	64.2	15.8	23.2[c]	39.0	25.2
	14-22	5.1	28.6	33.7	2.9	4.6	7.6	26.1
	22-06	7.2	9.4	16.6	3.7	4.6	8.4	8.2
7/29/79[a]	06-14	14.6	44.0[c]	58.6	10.8	31.0[c]	41.9	16.7
	14-22	5.5	16.9	22.4	5.2	13.8	18.9	3.5
	22-06	8.3	16.4	24.7	3.8	12.3	16.1	8.6

a. Samplers heated 3 min. at ca. 50°C following particulate collection.

b. Samplers not heated.

c. Ghia nylon used for all after-filters on this day.

d. NaCl-impregnated Whatman 41 used for all after-filters on this day.

e. Duralon nylon filters used for all after-filters on this day.

f. Total inorganic NO_3^- sampler minus particulate NO_3^- sampler results.

g. Power failure.

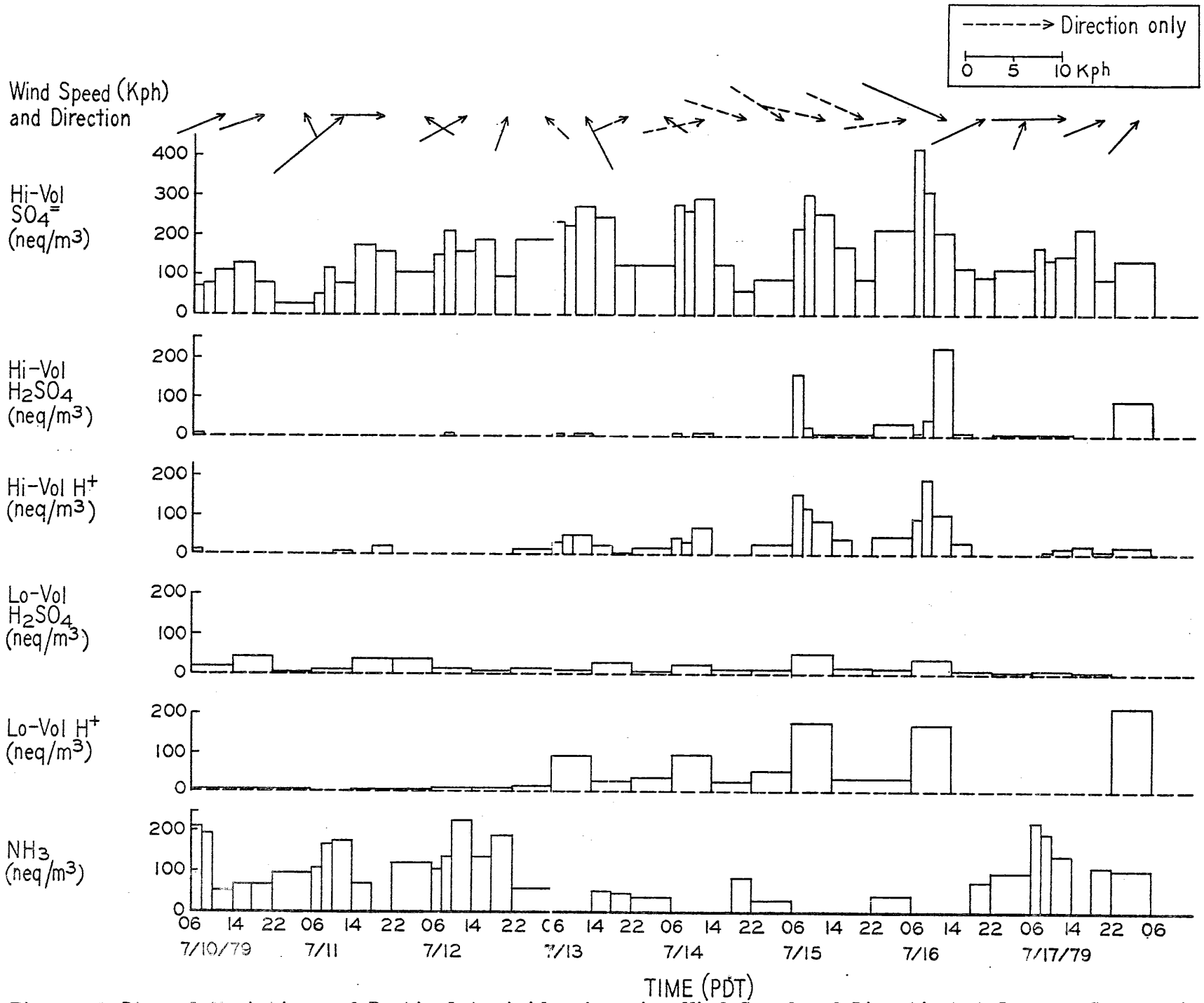


Figure 12 Diurnal Variations of Particulate Acids, Ammonia, Wind Speed and Direction at Lennox, California.

the arrowheads denoting the midpoints for eight-hour average values. Blanks indicate results below limits of detection. Samples showing the highest H_2SO_4 levels corresponded to W and NW winds during the preceding night and early morning hours (i.e., from the direction with strong sulfur oxide emissions). On these days, elevated levels of both H_2SO_4 and total strong acidity were observed with values up to 200 neq/m^3 (11 $\mu g/m^3$ as H_2SO_4).

Correlation coefficients for linear regression between the aerosol and gaseous constituents are shown in Table 23. For cases with $r \geq 0.5$, the regression equations are given in Table 24. For eight days of sampling the correlation between hi-vol H^+ and H_2SO_4 was relatively low ($r = 0.45$). Gaseous HNO_3 at Lennox ranged from below detection to 230 neq/m^3 (15 $\mu g/m^3$). A fraction of this HNO_3 adsorbed on particulate matter would contribute to the strong acidity measurement. The correlation coefficient between the neq H_2SO_4 plus HNO_3 and strong acid measurements was 0.82, providing limited support for the significance of HNO_3 in particulate acidity measurements.

The hi-vol and lo-vol H^+ measurements show moderate linear correlation ($r = 0.64$). The lo-vol samples yielded relatively high strong acid levels but low recoveries of H_2SO_4. Furthermore, the correlation between hi-vol H_2SO_4 and lo-vol H^+ was relatively high ($r = 0.83$). These results are consistent with the conversion of H_2SO_4 to NH_4HSO_4 on the filters since the acid sulfate is extracted with lower efficiency by benzaldehyde, but titrates as a strong acid. The average recovery of H^+ on the hi-vol sampler was 50% of that with the lo-vol with NH_3 denuder. The greater H^+ values on the lo-vol relative to hi-vol samples may be indicative of the effectiveness of the NH_3 denuder in preserving samples from neutralization by atmospheric ammonia. However, the negative correlation between hi-vol H^+ and NH_3 was only moderate ($r = -0.54$). As shown in Section IV, the denuder does not cause artifact strong acid formation in laboratory trials with $(NH_4)_2SO_4$ and $(NH_4)_2SO_4$-NH_4NO_3 mixture.

Based on the precision data, and decrease in recovery following an additional 30-days storage, the measures taken to preserve the atmospheric filter samples were insufficient to eliminate H_2SO_4 loss. One measure of such loss is provided by comparing corresponding H_2SO_4 and $SO_4^=$ levels since the latter represent an upper limit to the H_2SO_4 levels. At the H_2SO_4 maxima, the H_2SO_4 and H^+ levels were 80 to 110% of the $SO_4^=$ concentrations, suggesting for these samples, at least, losses are relatively minor. However partial extraction of NH_4HSO_4 by benzaldehyde may be influencing these results. In general, H_2SO_4 represented 10 to 20% of the sulfate.

Table 23 CORRELATION COEFFICIENTS[a] BETWEEN AEROSOL AND GASECUS POLLUTANTS SAMPLED AT LENNOX, CALIFORNIA

	Hi-Vol H_2SO_4[b]	Hi-Vol H^+	Hi-Vol $SO_4^=$	Hi-Vol NO_3^-	Hi-Vol NH_4^+	Lo-Vol H_2SO_4[c]	Lo-Vol H^+	Lo-Vol $SO_4^=$	NH_3	SO_2	HNO_3[d]	Hi-Vol $H_2SO_4 + HNO_3$
Hi-Vol H_2SO_4	1.0	0.45	0.23	- 0.43	- 0.21	0.19	0.83	0.31	- 0.22	0.24	0.17	--
Hi-Vol H^+		1.0	0.67	- 0.38	- 0.04	0.70	0.64	0.69	- 0.54	0.03	0.69	0.82
Hi-Vol $SO_4^=$			1.0	0.10	0.45	0.38	0.47	0.91	- 0.12	0.23	--	--
Hi-Vol NO_3^-				1.0	0.65	0.48	- 0.38	0.32	0.53	0.16	0.14	--
Hi-Vol NH_4^+					1.0	0.01	0.19	0.24	0.37	0.32	0.07	0.17
Lo-Vol H_2SO_4						1.0	0.22	0.55	0.30	- 0.12	0.64	--
Lo-Vol H^+							1.0	0.41	0.02	0.54	0.45	0.71
Lo-Vol $SO_4^=$								1.0	- 0.26	0.03	0.58	--
NH_3									1.0	0.20	0.18	0.05

a. Pearson's product moment correlation coefficient, r.

b. "Hi-Vol" indicates high volume respirable particulate sampler.

c. "Lo-Vol" indicates low volume respirable particulate sampler.

d. Measured by the difference technique.

Table 24 LINEAR REGRESSION ANALYSIS OF AEROSOL AND GASEOUS POLLUTANTS SAMPLED AT LENNOX, CALIFORNIA*

y	x	units of y	units of x	b	a	r	n**	p†††
LV H^+†	HV H_2SO_4	$\mu g/m^3$	neq/m^3	0.074	1.78	0.84	14	1.00
HV H^+††	HV $SO_4^=$	$\mu g/m^3$	$\mu g/m^3$	0.35	- 1.16	0.66	34	1.00
LV H_2SO_4	HV H^+	$\mu g/m^3$	neq/m^3	0.013	0.46	0.70	18	1.00
HV H^+	LV H^+	$\mu g/m^3$	$\mu g/m^3$	0.35	0.58	0.64	12	0.98
LV $SO_4^=$	HV H^+	$\mu g/m^3$	neq/m^3	0.11	8.66	0.69	19	1.00
HV H^+	NH_3	$\mu g/m^3$	$\mu g/m^3$	- 0.23	1.30	- 0.54	12	0.93
HNO_3	HV H^+	neq/m^3	neq/m^3	1.36	36.8	0.69	15	1.00
HV H_2SO_4 + HNO_3	HV H^+	neq/m^3	neq/m^3	2.04	35.5	0.82	16	1.00
LV $SO_4^=$	HV $SO_4^=$	$\mu g/m^3$	$\mu g/m^3$	1.41	1.23	0.91	23	1.00
HV NO_3^-	NH_3	$\mu g/m^3$	$\mu g/m^3$	0.60	0.56	0.53	22	0.99
LV H_2SO_4	LV $SO_4^=$	$\mu g/m^3$	$\mu g/m^3$	0.068	0.04	0.55	22	0.99
LV H_2SO_4	HNO_3	$\mu g/m^3$	$\mu g/m^3$	0.09	0.50	0.64	23	1.00
LV H^+	SO_2	$\mu g/m^3$	ppm	206	- 0.29	0.54	10	0.89
LV H^+	HNO_3	$\mu g/m^3$	$\mu g/m^3$	0.35	1.92	0.50	14	0.93
LV H^+	HV H_2SO_4 + HNO_3	$\mu g/m^3$	neq/m^3	0.025	1.00	0.71	14	1.00
LV $SO_4^=$	HNO_3	$\mu g/m^3$	$\mu g/m^3$	0.62	9.14	0.58	23	1.00

* $y = a + bx$

** number of data pairs

† LV = low-volume sampler

†† HV = high-volume sampler

††† Significance of the difference of the correlation coefficient, r, from zero.

2. Claremont

As shown in Figure 13, the maximum H_2SO_4 levels observed at Claremont were about half those at Lennox. There is no correlation between H^+ and H_2SO_4 levels ($r = -0.24$ and 0.09 for hi-vol and lo-vol samples, respectively). Gaseous HNO_3 at this site ranged up to 1200 neq/m^3 (76 µg/m^3). The diurnal variations for the HNO_3 concentration, measured by the difference method, are also shown in Figure 13. The addition of HNO_3 to the H_2SO_4 level improves the correlation with particulate H^+, but the correlation coefficient remains relatively low ($r = 0.44$).

The concentration of gaseous NH_3 at Claremont exceeded that at Lennox exhibiting a pronounced diurnal maximum during early morning hours. Negative correlations between NH_3 and H^+ or H_2SO_4 with the unprotected respirable particulate hi-volume sampler might be expected. The observed correlation coefficients were $r = -0.52$ and $r = -0.05$ for H^+ against NH_3, and H_2SO_4 against NH_3, respectively. Thus, while neutralization of airborne H_2SO_4 aerosols by atmospheric NH_3 is highly likely, no correlation between the NH_3 level at the sampling site and the H_2SO_4 concentration is seen.

The sum of the equivalents of sulfate and nitrate may be compared to the total of H^+ and ammonium ions at both sites. For 16 sampling periods the cation:anion ratio of equivalents averaged 0.68 ± 0.21. Even during periods of elevated H_2SO_4 and/or H^+, the ratio remained within the variation shown. Thus other water-soluble cations (e.g., Na^+, K^+, Ca^{+2}) contribute to the particulate matter.

E. Measurement of Nitric Acid

Atmospheric sampling was done by the Okita and Spicer methods with and without filter heating. Figure 14 compares atmospheric HNO_3 results on heated, NaCl/W41 and nylon filters. Consistent with the laboratory findings for samples with < 500 µg NO_3^-/filter (Section III), results on the NaCl/W41 filters (i.e., the Okita method) are slightly higher than on nylon.

Measurement of HNO_3 by filter collection is subject to positive error if particulate nitrate is lost from the Teflon prefilter. However, HNO_3 measured by TIN minus PN ("HNO_3 by difference") should be independent of such error. Figure 15 compares "HNO_3 by difference" and HNO_3 by unheated filter collection. The results show high correlation. The higher values by filter collection are consistent with the loss of nitrate from the prefilters. The same comparison, but with heated filters, is shown in Figure 16. Again, results correlate well, with higher values by filter collection. However, there is greater average deviation from "HNO_3 by difference" compared to results without heating, implying increased NO_3^- loss from the prefilter.

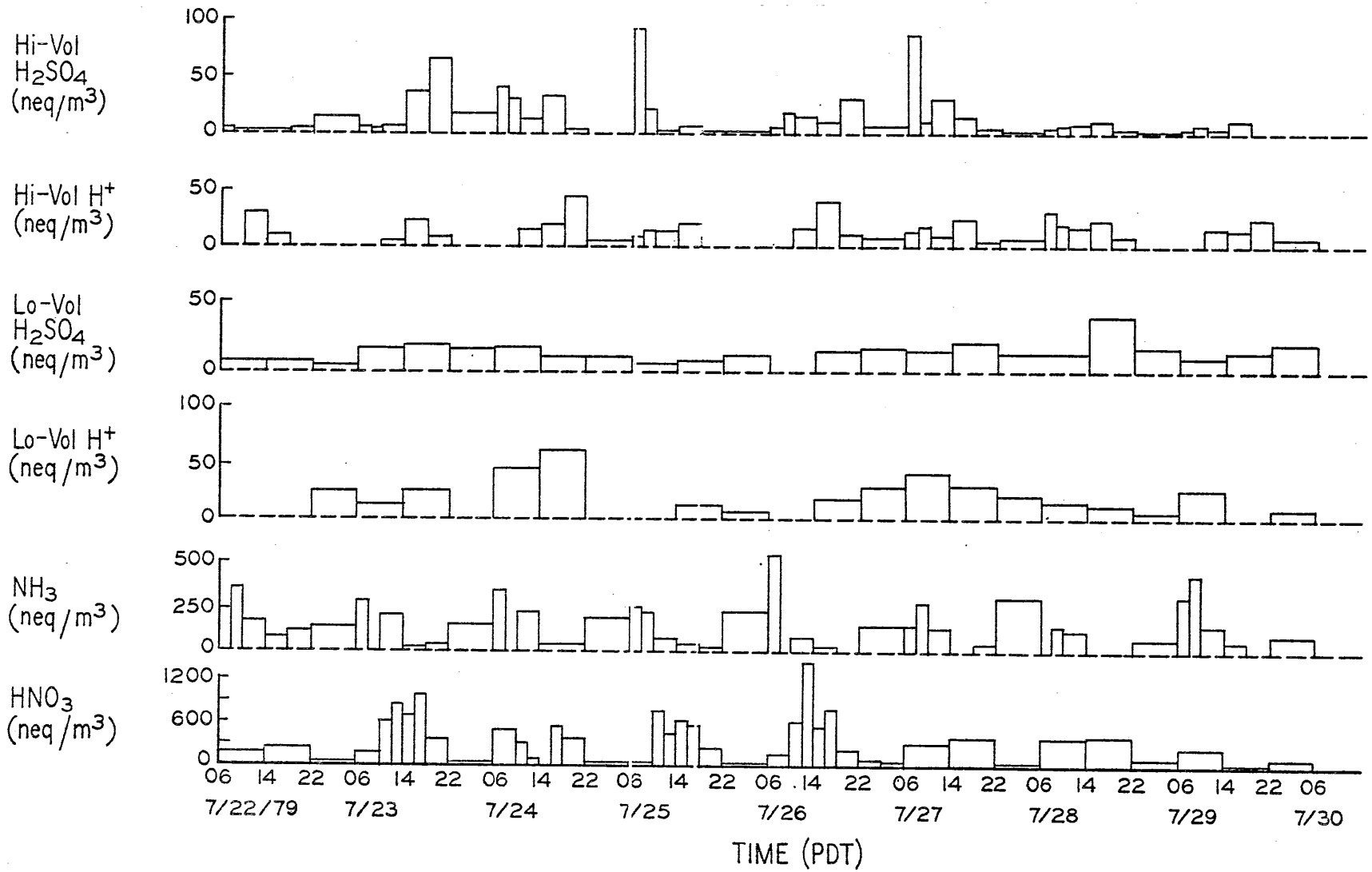


Figure 13 Diurnal Variations of Particulate Acids, Ammonia and Nitric Acid at Claremont, California

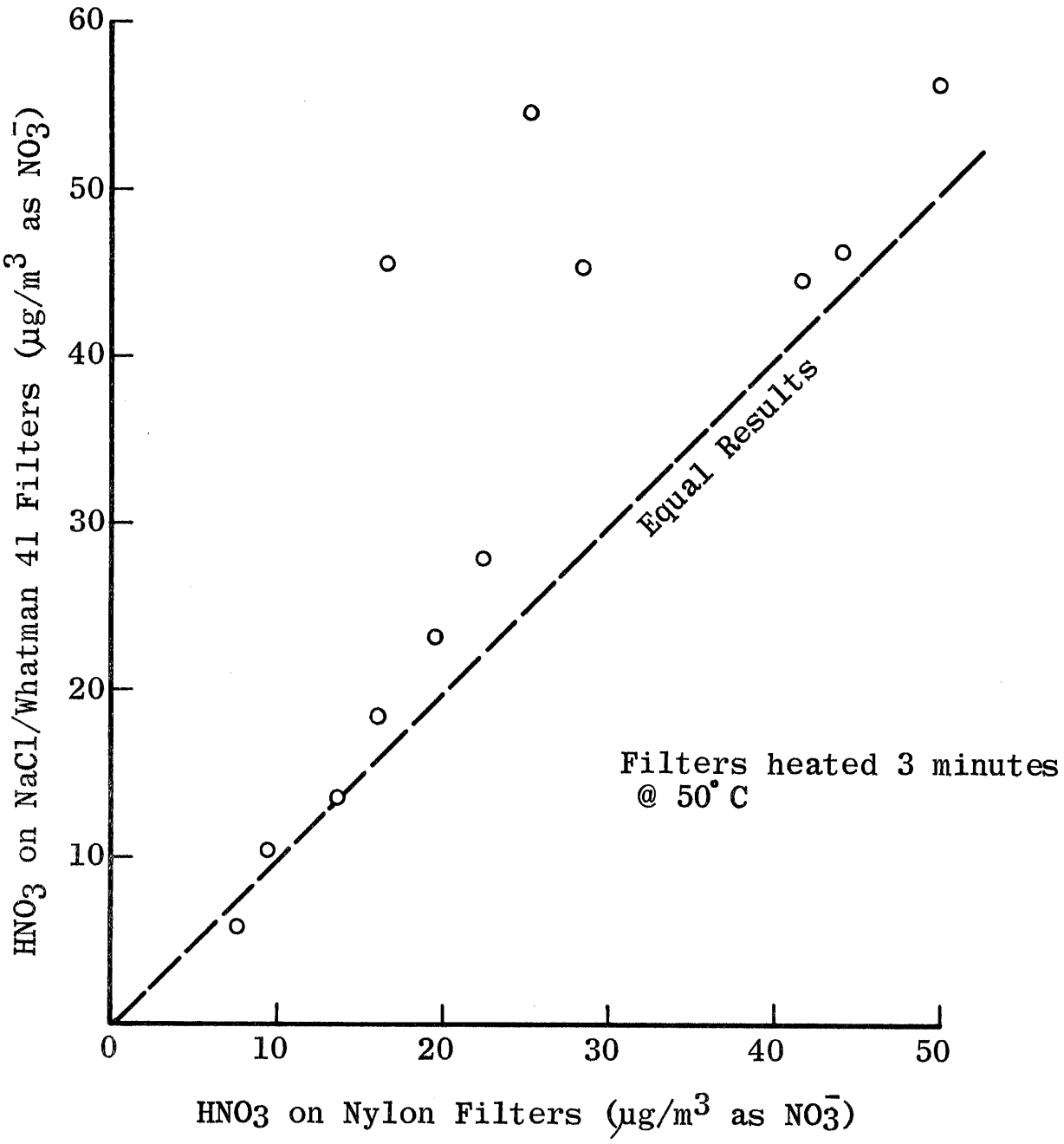


Figure 14 Atmospheric HNO_3 Collection on Nylon vs. NaCl/Whatman 41 Filters

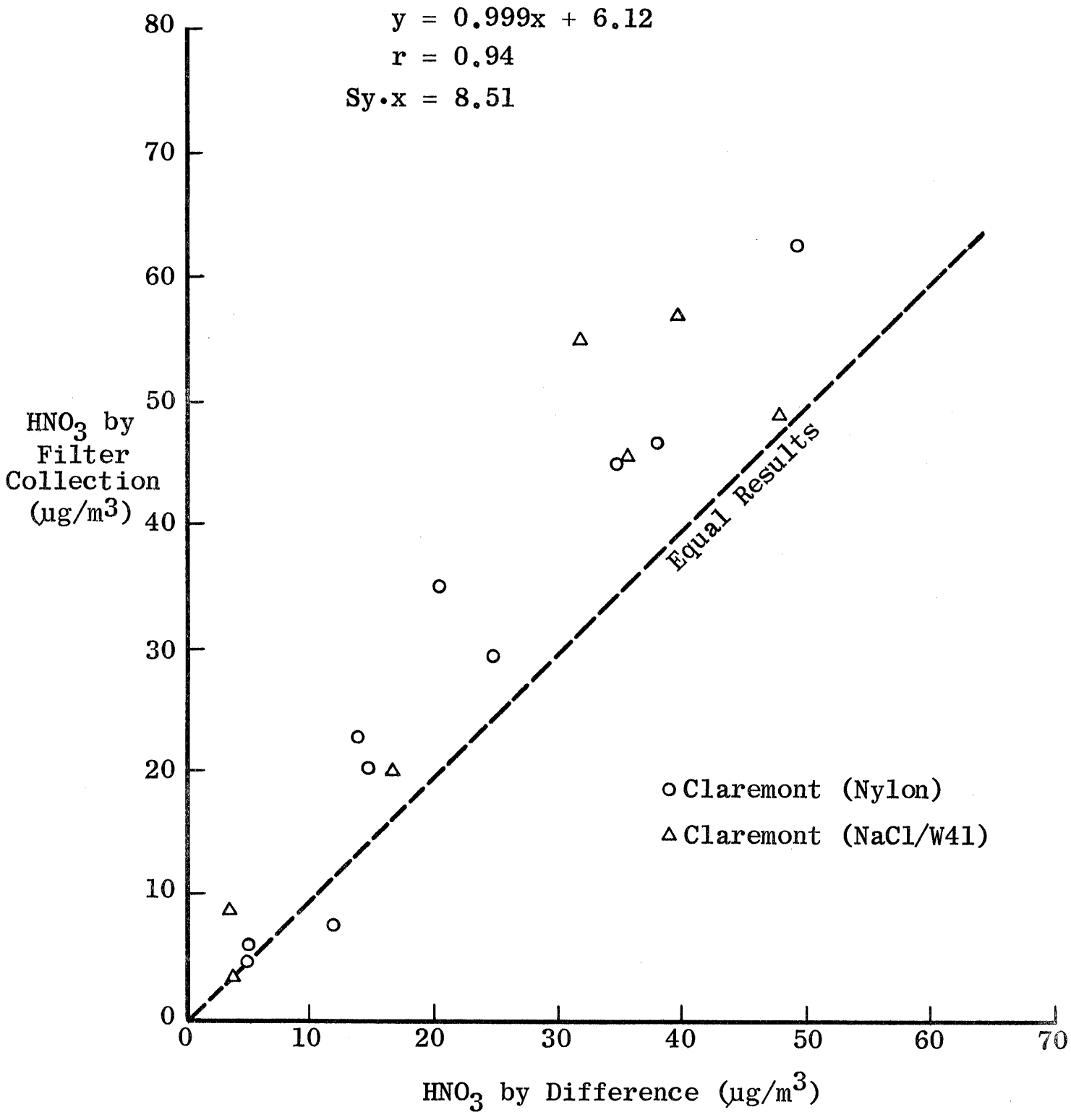


Figure 15 Comparison of HNO_3 by filter collection and "by Difference" Using Unheated Samplers

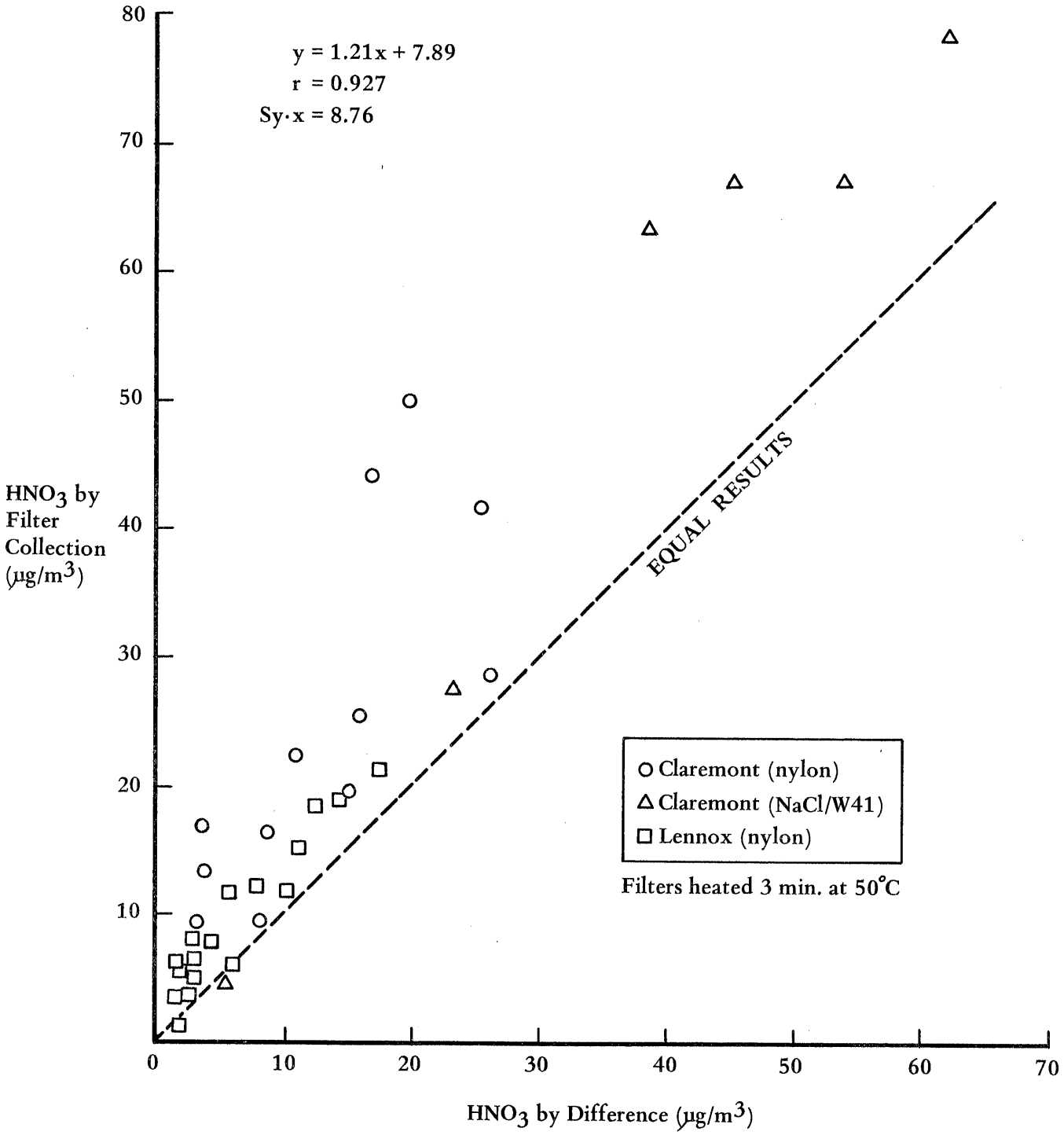


Figure 16 Comparison of HNO_3 by Filter Collection and "by Difference" Using Heated Samplers

In Section III losses of HNO_3 up to about 25% were shown on Teflon prefilters bearing atmospheric particulate matter, the level increasing with particulate loading. This produced a corresponding negative error in nitric acid measurements by the filter collecting technique using these prefilters. In the present atmospheric trials, while TSP measurements were not made, such negative errors appear to be offset by losses of volatile particulate nitrate from the prefilter. Assuming a TSP of 100 $\mu g/m^3$, the atmospheric particulate matter collected in 2, 4 and 8-hour samples equals 240, 480 and 960 µg/filter. From Figure 1, only the eight-hour samples would show retentions > 10%. However, in locations with relatively high HNO_3 levels but low particulate nitrate, errors in HNO_3 measurement due to retention of the acid on particulate matter may be detectable.

Figure 17 compares "HNO_3 by difference" to simultaneous HNO_3 by measurements by a long-path Fourier transform infrared (FTIR) technique, here considered to be the reference method. FTIR data were obtained by averaging results obtained at 15 to 30-minute intervals. The ratio of means, HNO_3 by difference : HNO_3 by FTIR was 1.2, implying an average accuracy of 80% for the difference method. However, the linear correlation coefficient was low ($r = 0.2$). Because of the generally higher results for "HNO_3 by difference" only lower limit estimates of the error in the HNO_3 values by filter collection can be inferred from comparisons with "HNO_3 by difference" as in Figures 15 and 16.

These results may be considered viz-a-viz the 88% efficiency measured for the denuder for HNO_3 removal. A 12% penetration of HNO_3 should yield high PN values. Since PN represented, on average, nearly 50% of the TIN, this should yield about 12% low "HNO_3 by difference" values. Comparing "HNO_3 by difference" to FTIR results, results with the former suggest that opposing sources of error (e.g., loss of particulate nitrate) more than offset that caused by HNO_3 penetration. While laboratory studies could not demonstrate loss of 0.1 to 3 µm PN particles in the denuder, loss of > 3 µm nitrate-containing particles remains a possible explanation for the high "HNO_3 by difference" results.

F. Negative Errors in Particulate Nitrate Sampling

Although Teflon and quartz filters yield low levels of artifact particulate nitrate, particulate nitrate sampling with such inert filters is subject to negative error because of volatilization of NH_4NO_3 and reactions liberating HNO_3. Figure 18 is a scatter diagram of nitrate against H^+ results both obtained from two to eight-hour samples collected with the respirable particulate hi-vol sampler and acid-washed quartz filters. No correlation is evident suggesting that other factors control the observed NO_3^- levels.

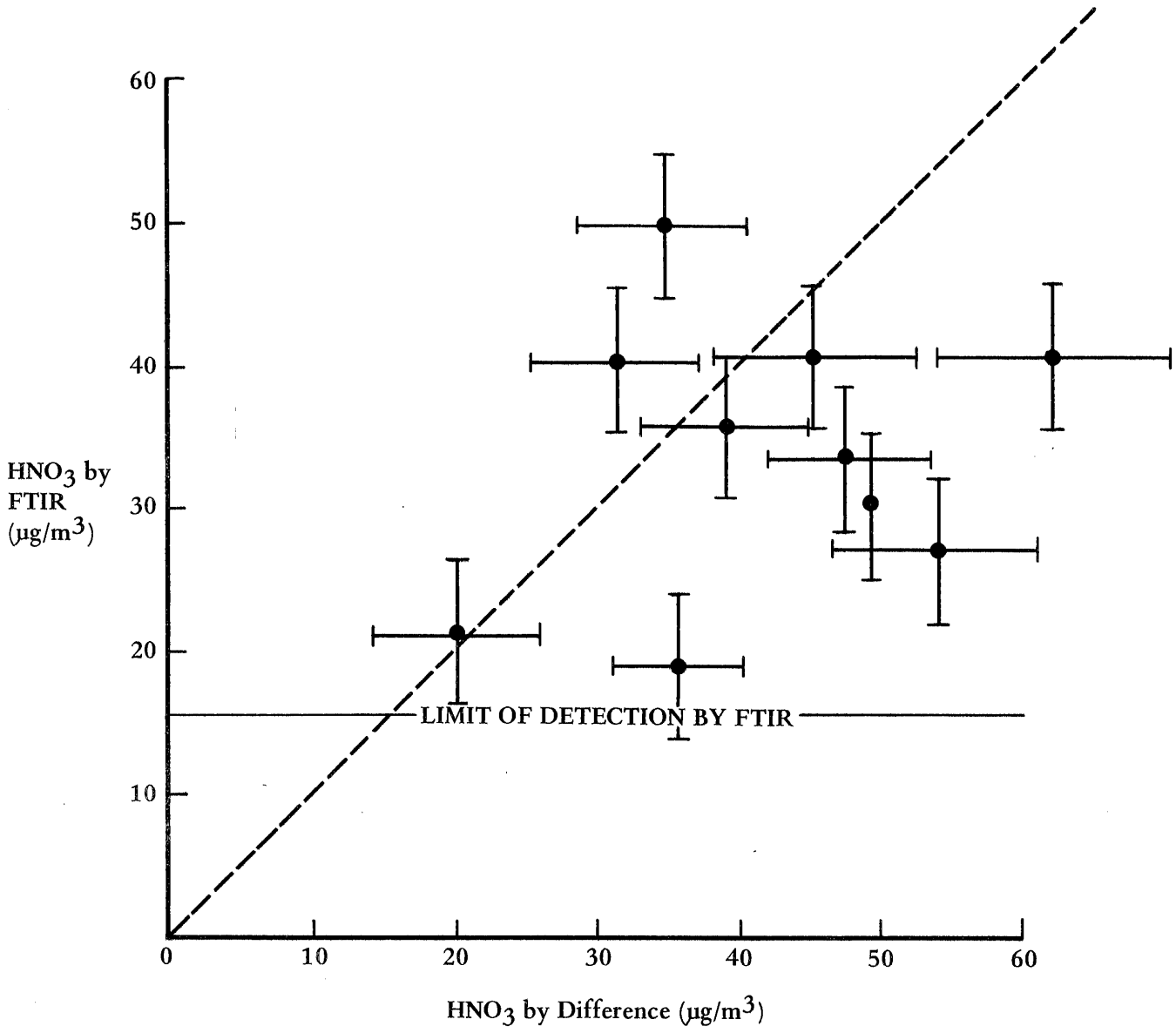
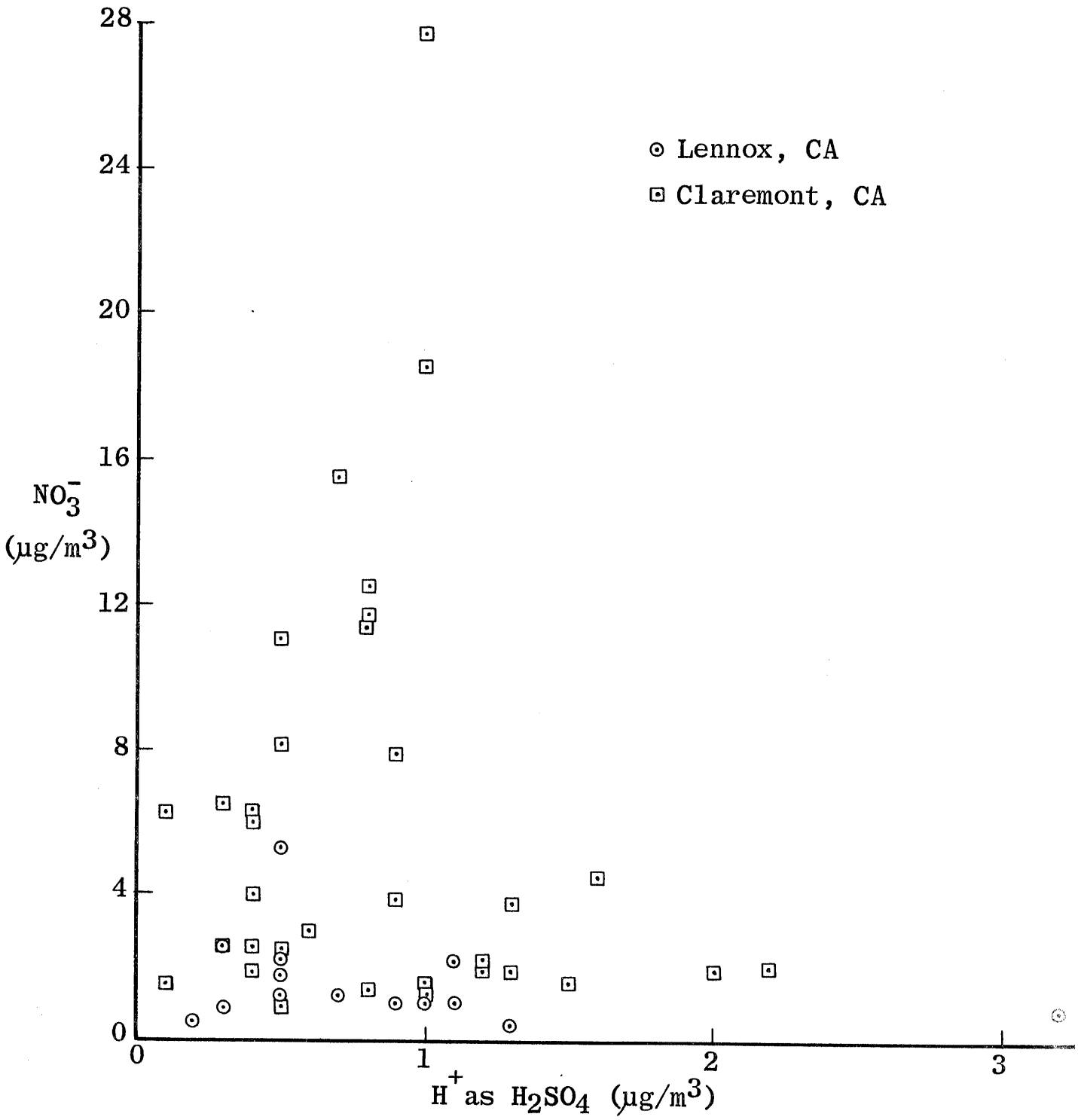


Figure 17 Comparison of HNO_3 by Long Path Fourier Transform Infrared (FTIR) and "by Difference"

Figure 18

SCATTER DIAGRAM OF NITRATE AGAINST STRONG ACID CONCENTRATIONS FOR HI-VOL SAMPLES COLLECTED ON QUARTZ FIBER FILTERS



A somewhat more specific evaluation of the effect of particulate acids on nitrate loss is provided by examining the results obtained with the particulate nitrate sampler. The nitrate collected on the Teflon filter downstream of the acid gas denuder is subject to losses both from volatilization and particulate acid-nitrate salt reactions. Gaseous acid-nitrate salt reactions would be negligible because of the use of the acid gas denuder. The nitrate lost by either mechanism was collected on the reactive after-filter. The proportion of the total 8-hour average total particulate nitrate retained on the Teflon filter is plotted against simultaneous strong particulate acidity values in Figure 19. Only data from Lennox, California were examined because of the high particulate acidity levels observed at that site. For concentration of strong acid which reached nearly 11 $\mu g/m^3$ (expressed as H_2SO_4) and nitrate levels up to 9 $\mu g/m^3$ on the prefilters, a correlation coefficient of -0.75 was observed, providing some support for the significance of this loss mechanism. By contrast the analogous plot against 1/T (°K) showed no correlation ($r = -0.15$) implying that volatilization was not the dominant source of particulate nitrate loss at this site.

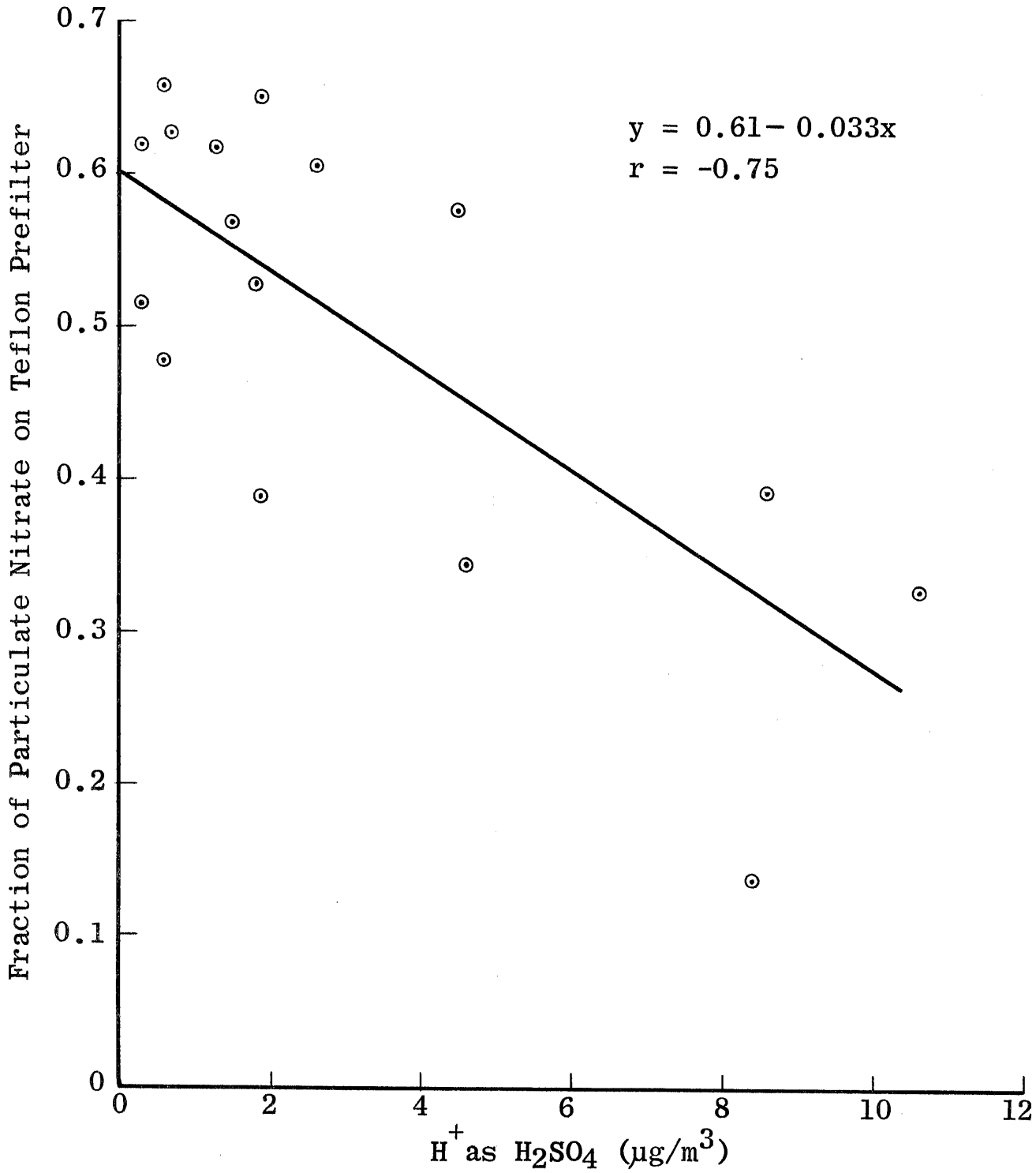
The extent of the loss of particulate nitrate from Teflon filters during atmospheric sampling was estimated by comparing the nitrate results on Teflon prefilters with those from simultaneously collected PN samples using the acid gas denuder (i.e., the sum of the NO_3^- on the Teflon filter and reactive after-filter). With unheated samples, the results (Figure 20) fall into two sets, one with reasonable agreement between techniques and the second, with much lower prefilter results. The first set corresponds to samples collected during night and morning hours. The samples deviating badly were collected with ambient temperatures in the range 29 to 35°C and relative humidities about 30%. Under these conditions, more than 50% of the nitrate appears to be lost from the Teflon prefilters. Figure 21 makes the same comparison using heated samplers. The results for all samples are similar to those in Figure 20 when the ambient temperature was high, indicating that most of the nitrate on the prefilter has been lost. Because of possible loss of PN in the denuder, errors inferred for the prefilters are minimum values. We conclude that the PN sampler (Figure 3) gives a more reliable measure of particulate nitrate than collection on Teflon filters.

G. Positive Errors in Particulate Nitrate Sampling with Glass Fiber Filters

Artifact particulate nitrate formation can be a major source of interference with glass fiber, cellulose, and cellulose ester filters. Earlier studies comparing atmospheric nitrate collection with six filter types to the results from laboratory exposures of these filters to nitrogen oxides, suggested that retention of nitric acid, rather than NO_2, was the dominant source of artifact particulate nitrate formation.[30] Atmospheric sampling of nitrates

Figure 19

SCATTER DIAGRAM OF THE PROPORTION OF PARTICULATE NITRATE RETAINED BY A TEFLON FILTER AGAINST THE PARTICULATE STRONG ACID CONCENTRATION AT LENNOX, CA



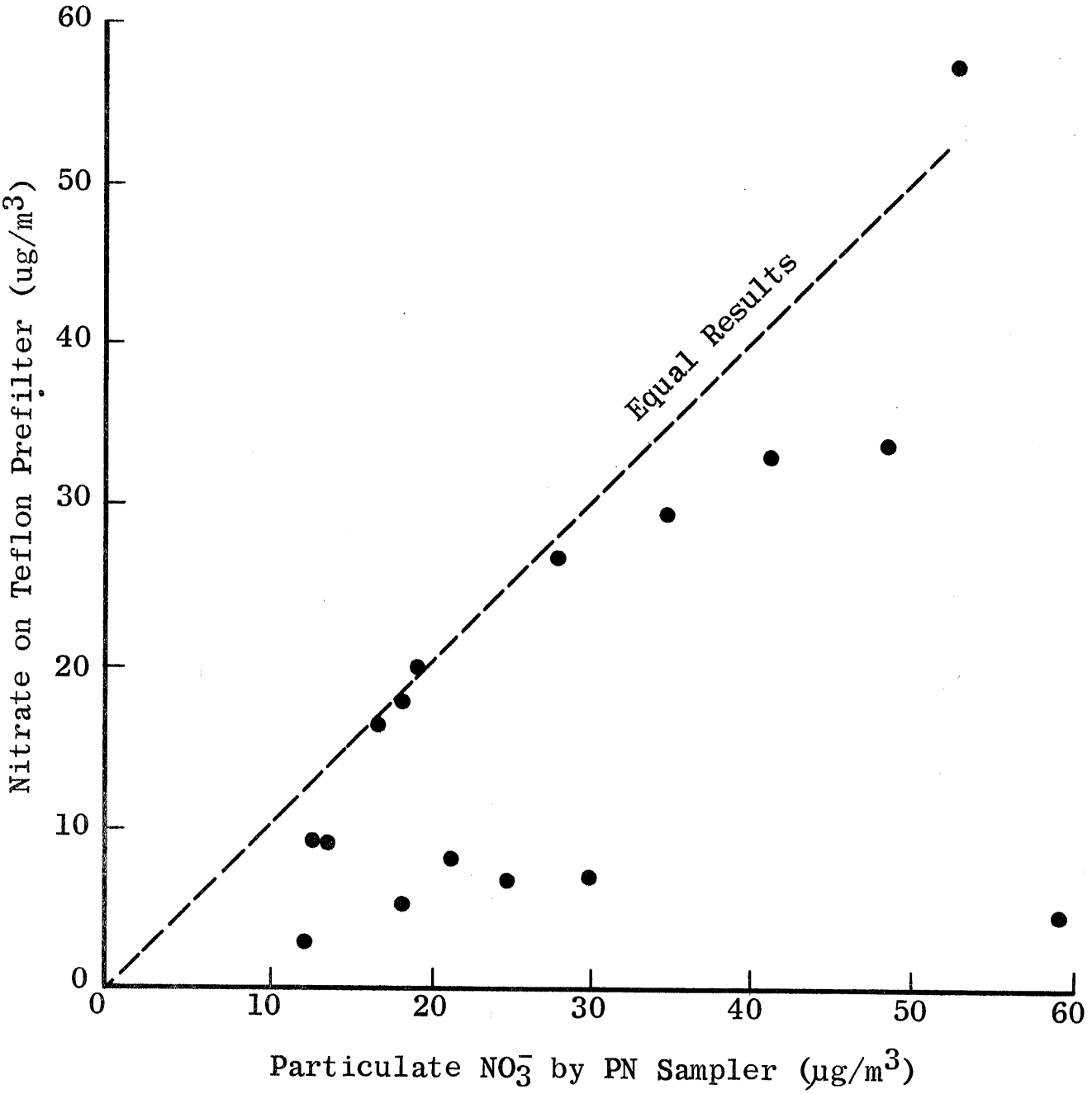


Figure 20 Comparison of Nitrate Levels on Teflon Prefilters with Particulate Nitrate Measured with the PN Sampler (Samplers Unheated)

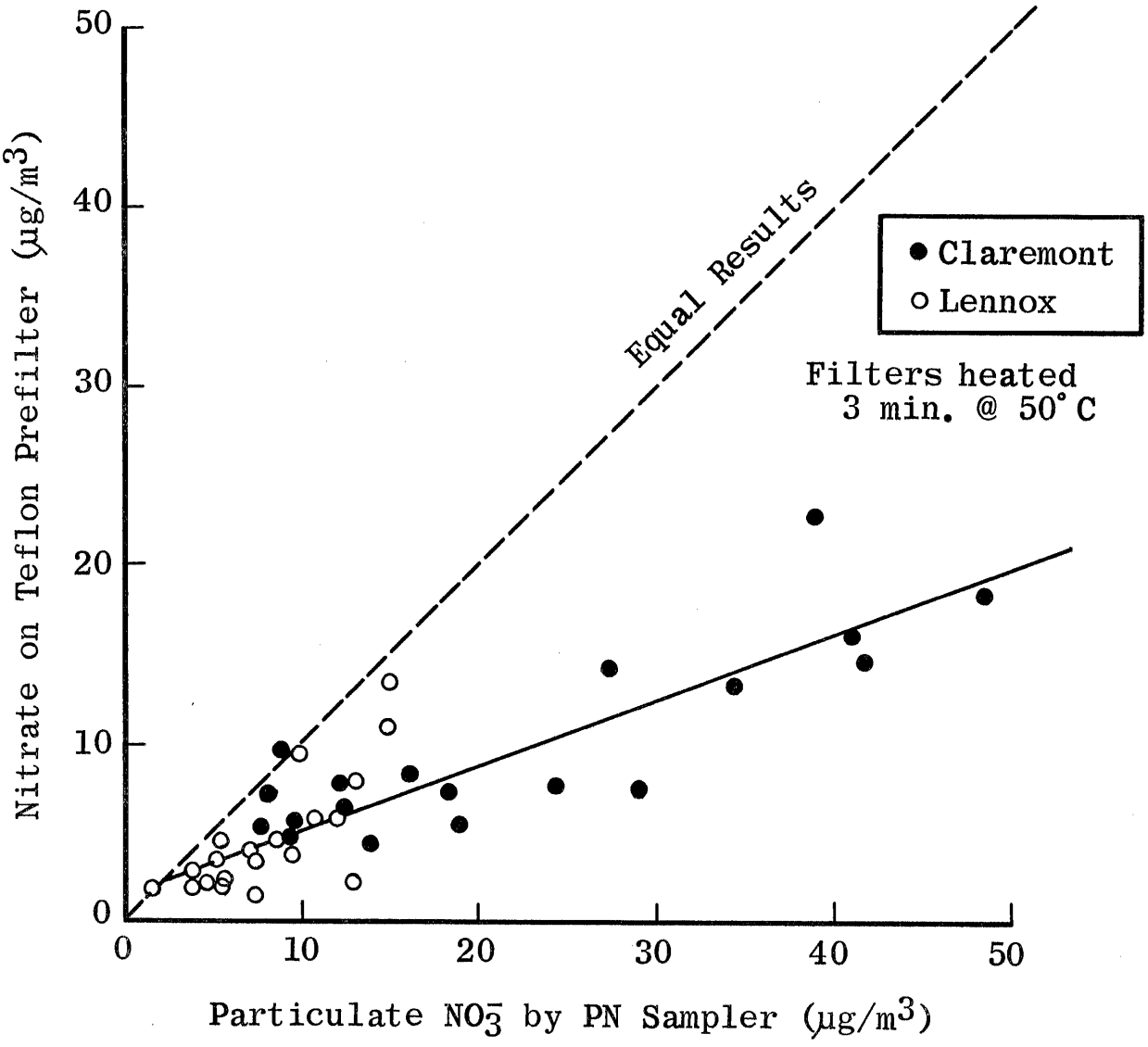


Figure 21 Comparison of Nitrate Levels on Teflon Prefilters with Particulate Nitrate Measured with the PN Sampler (Samplers Heated)

with Gelman A (pH = 7.6) glass fiber filters demonstrated that the concentrations measured were equal to the TIN at low (< 4 $\mu g/m^3$) HNO_3 levels.

In the present study this evaluation was extended to higher HNO_3 and TIN levels. Figure 22 compares TIN values to nitrate concentrations obtained with 47 mm Gelman A (pH = 7.6) glass fiber filters sampling for two to eight hours at 25 Lpm. Again, the results are not significantly different. Since NO_2 at ambient levels is not collected on nylon or NaCl/W41 filters,[1,13,31] these findings confirm that nitric acid is the principal source of artifact particulate nitrate on glass fiber filters, at least at the locations studied. Similar behavior would be expected with 24-hour samples using the more alkaline (pH $\geq$ 9) glass fiber filters typically employed in high-volume samplers.

H. Atmospheric Nitrate and HNO_3 Levels at Claremont, California

Figure 23 compares the diurnal variations of PN with those for HNO_3 (by difference) and O_3 at Claremont. HNO_3 and O_3 show similar diurnal patterns consistent with previous reports using real-time analyzers.[32] The diurnal maximum for particulate NO_3^- occurred earlier in the day, compared to those for HNO_3 and O_3, again consistent with earlier results.[33]

I. Intermethod Comparison of Techniques for Atmospheric Ammonia Determination

Atmospheric NH_3 results obtained by the oxalic acid-impregnated filter technique are compared to those by FTIR in Figure 24. FTIR data are averages of results obtained at 15 to 20-minute intervals for comparison with the two-hour integrated values by the filter method. The results are highly correlated, but FTIR values are consistently higher. The mean difference in the data sets is 2.5 ± 0.5 $\mu g/m^3$ (as NH_4^+). Assuming the FTIR results to be correct, the present comparison suggests that 1) NH_3 may be lost by adsorption and/or reaction on the glass fiber prefilter and its particulate matter, and 2) that such loss dominates over the opposing source of error, reactions of ammonium salts on the prefilter liberating NH_3. Alternatively, the impregnated filters may be inefficient for NH_3 collection at very low concentrations.

J. The Role of Ammonia in Nitrate Chemistry

Atmospheric ammonium nitrate is believed to exist in equilibrium with NH_3 and HNO_3:

$$NH_4NO_3(s) \rightleftarrows NH_3(g) + HNO_3(g)$$

$$K = (NH_3)(HNO_3)$$

The equilibrium "constant" is dependent on temperature and, perhaps on relative humidity as well.[7] High concentrations of ammonia

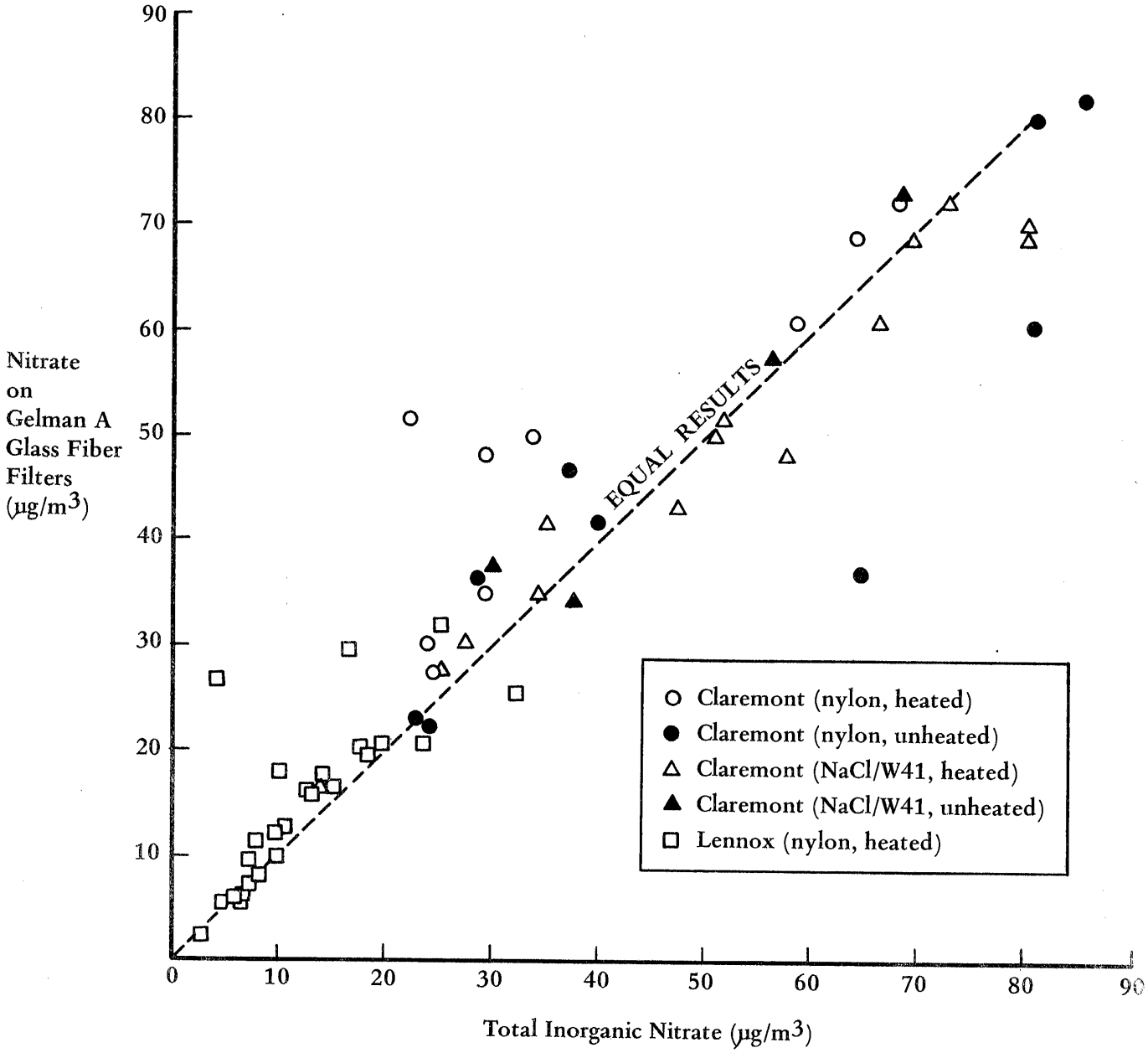


Figure 22 Glass Fiber Filters as Total Inorganic Nitrate Samplers

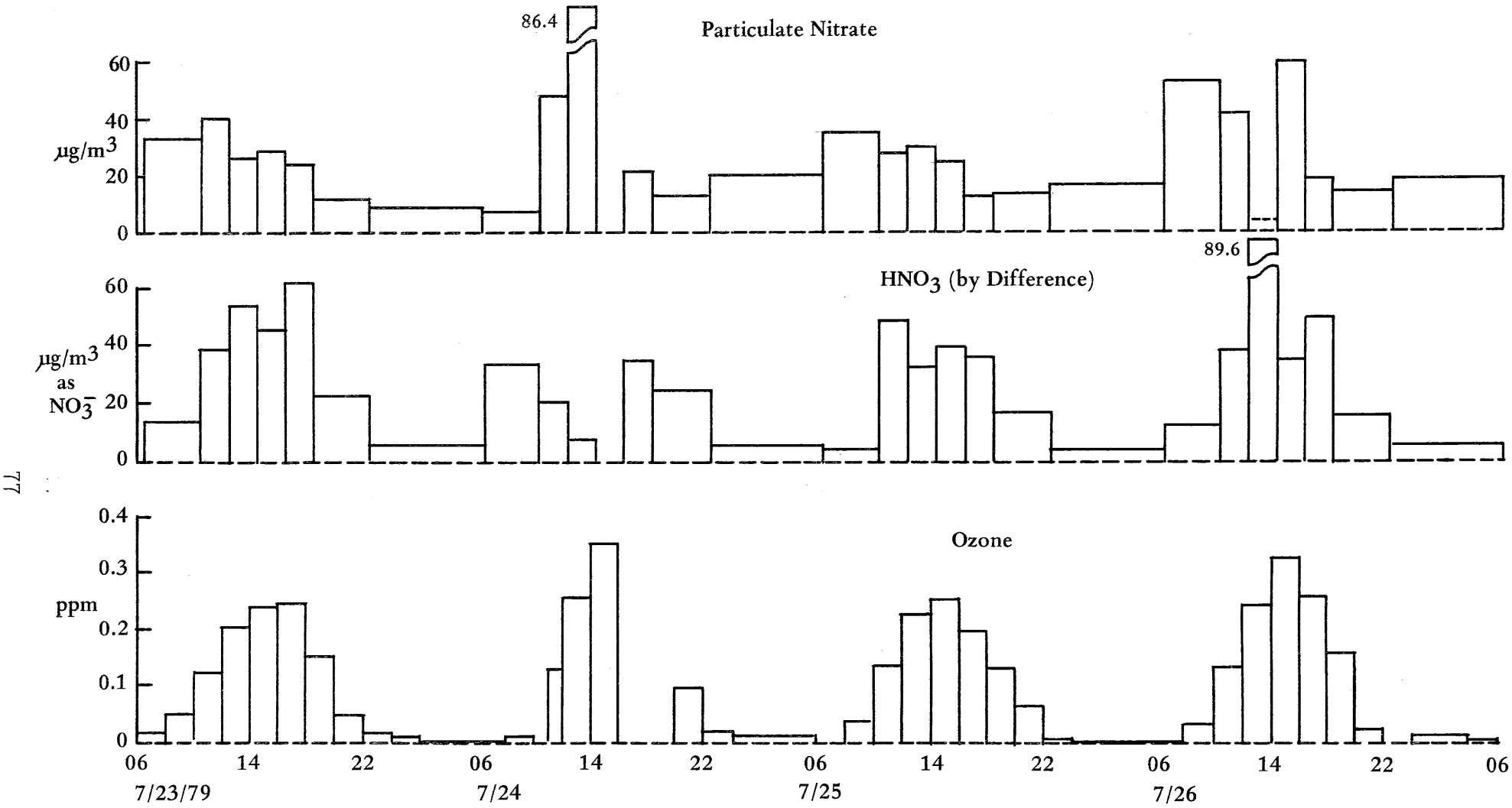
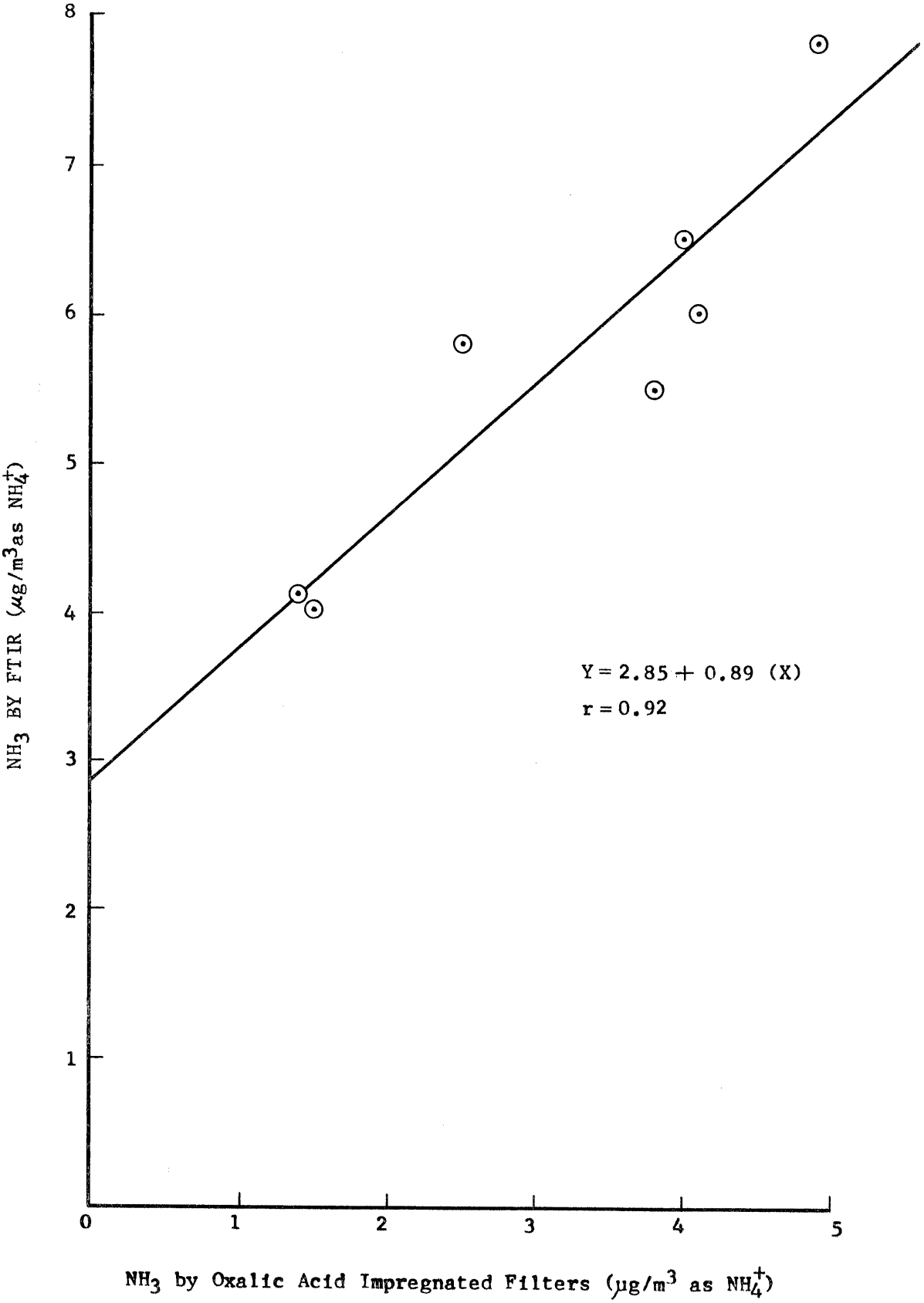


Figure 23 Diurnal Variations of HNO_3, Particulate Nitrate and Ozone at Claremont, California

Figure 24 COMPARISON OF NH_3 BY LONG PATH FOURIER TRANSFORM INFRARED (FTIR) AND BY OXALIC ACID-IMPREGNATED FILTERS



should lead to low observed HNO_3 levels. Figure 25 is a scatter diagram of HNO_3 concentration against NH_3. While the negative correlation coefficient is relatively low, -0.47, the trend supports expectations.

The NH_3 and HNO_3 data may be used to calculate the above equilibrium constant. Since at low concentrations the NH_3 and HNO_3 are probably below the equilibrium concentration based on saturation with respect to NH_4NO_3 dissociation, the resulting concentration product would provide only lower limit values for K. Figures 26 and 27 plot the concentration product against relative humidity and 1/T (°K) for cases with products > 5(ppb)^2. The dissociation constant is highest at low R.H. and high temperature. These findings are consistent with the preceding results which showed the greatest loss of NO_3^- from prefilters at the highest temperatures and lowest R.H. Figure 25 also shows results segregated by R.H. range. At constant temperature, lower R.H. seems to favor higher K values. The median concentration product for the data plotted was 15.8 (ppb)^2. This value is similar to those reported by Stelson et al.[2] and compares to the value $\geq$ 21 (ppb)^2 reported in Section III for volatilization of pure NH_4NO_3 at 50 and 80% R.H. and 21°C.

Figure 13 noted elevated early morning levels of NH_3. It follows that the observed diurnal variation for HNO_3, with its midday maximum, might reflect, at least in part, the decreased concentration of NH_3 rather than a photochemical origin for HNO_3.

K. The Composition of Atmospheric Particulate Nitrate

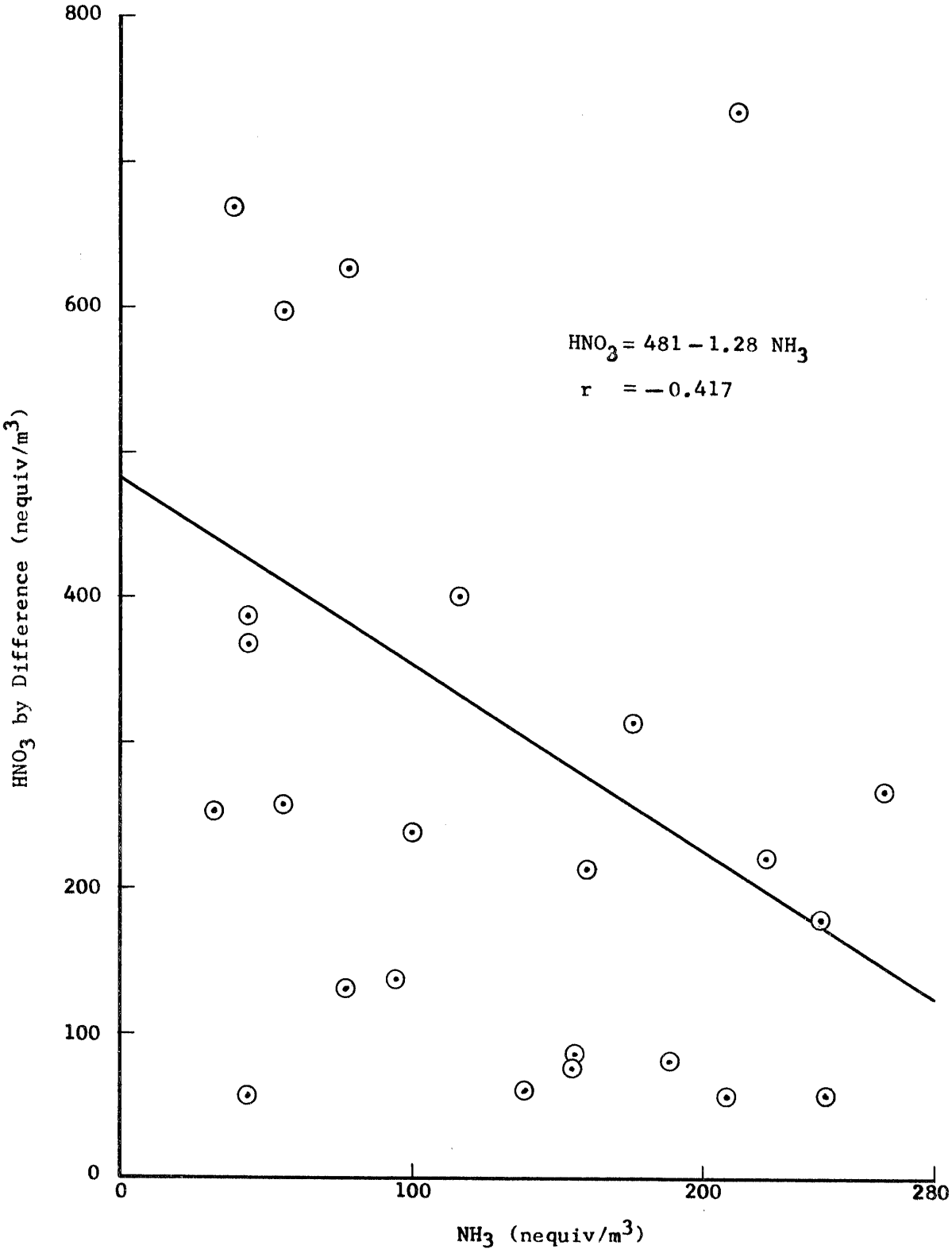
The preceding discussion of the role of NH_3 in particulate nitrate formation provides support for the significance of NH_4NO_3 in atmospheric particulate matter. In addition to this salt, nitrate may be present as the sodium (or other metal) salt,* as adsorbed HNO_3 or as addition compounds, e.g., $NH_4NO_3 \cdot 2HNO_3$.[36] The latter two would contribute to particulate acidity. It was shown in Section V D that the correlation between total strong particle acids and the sum of particulate H_2SO_4 and gaseous HNO_3 was substantially better than between strong acid and H_2SO_4 alone. This was interpreted as support for the significance of adsorbed HNO_3. Additional support was previously reported using temperature-programmed electron spectroscopy for chemical analysis (ESCA).[36] Volatilization rates for nitrate and ammonium from atmospheric samples were greatly in excess of those from pure NH_4NO_3.

The chemical nature of particulate nitrate may also be revealed by the pattern of nitrate collection following passage through the diffusion denuder. If this nitrate were non-volatile, all

---

* Reference 34 discusses techniques to distinguish NH_4NO_3 from $NaNO_3$ and their application in atmospheric sampling.

Figure 25. ATMOSPHERIC NITRIC ACID AGAINST AMMONIA CONCENTRATIONS AT CLAREMONT



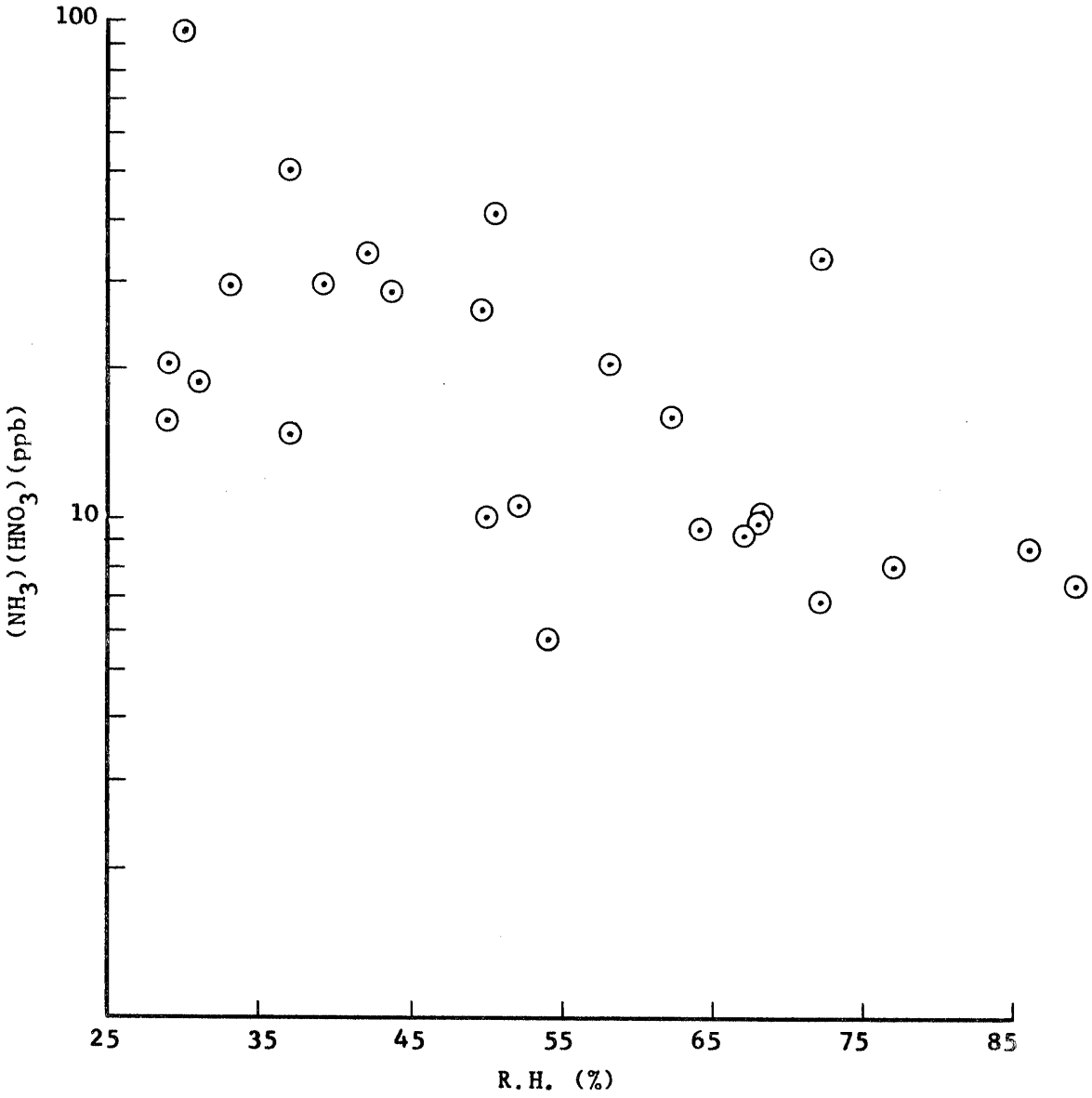
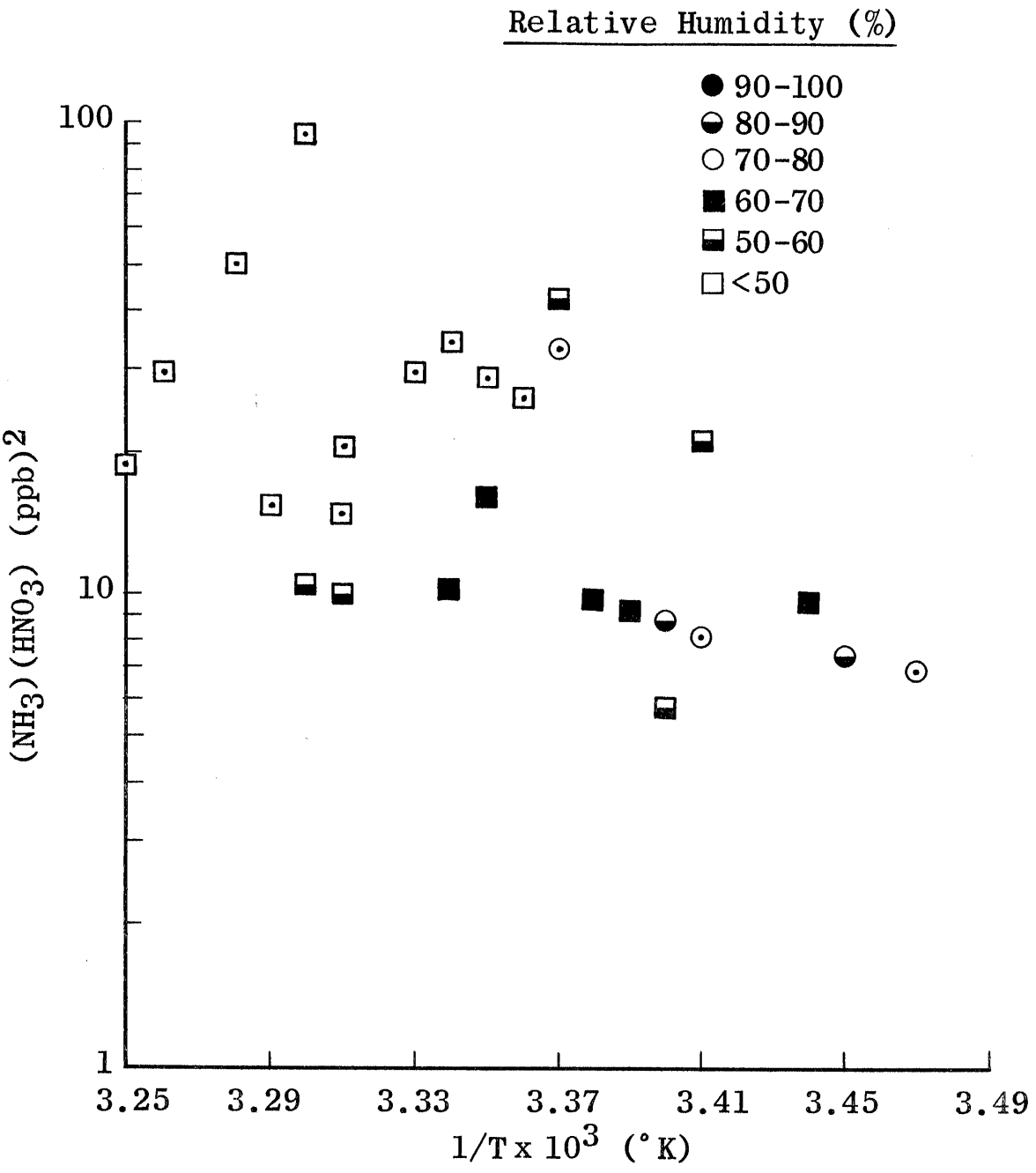


Figure 26 RELATIVE HUMIDITY DEPENDENCE OF THE CALCULATED NH_4NO_3 DISSOCIATION CONSTANT.

Figure 27

TEMPERATURE DEPENDENCE OF THE CALCULATED NH_4NO_3 DISSOCIATION CONSTANT



would remain on the Teflon filter (excepting the HNO_3 liberated by reaction of the nitrate salts with particulate acids). Figure 28 plots the fraction of the nitrate retained by the Teflon prefilter against the ambient HNO_3 concentration measured by the difference method. The data plotted are for the three episodes, 7/24, 7/25, and 7/26/80 when no filter heating was employed. In spite of the removal of 88% of the HNO_3 by the denuder, the fraction of nitrate retained on the prefilter is negatively correlated with the HNO_3 level. Assuming 12% penetration of HNO_3 through the denuder (see Section III), the mean nitrate expected on the after-filter due only to the HNO_3 is 2.9 $\mu g/m^3$, compared to an observed mean of 14.4 $\mu g/m^3$ (n = 19). Thus, on average, the observed NO_3^- on the after-filter is five times that explainable by atmospheric HNO_3 penetration. These results are consistent with the significance of particulate-bound HNO_3 which is easily desorbed when gaseous HNO_3 is removed.

However, these observations lend themselves to alternate interpretations. Figure 29 shows a similar plot against average ambient temperature for the same episodes. Data points are also coded for R.H. range. Clearly high temperature and low R.H. can also be related to low retention of nitrate on the filters. Such an observation is qualitatively consistent both with loss of adsorbed HNO_3 (or dissociation of HNO_3-NH_4NO_3 adducts) and NH_4NO_3 dissociation on the prefilter. The latter should also be favored by elimination of HNO_3. Further work is needed to elucidate the contributions of the various nitrate compounds to atmospheric particulate matter especially as regards the role of particle-bound nitric acid.

L. Conclusions

1. Significant levels of H_2SO_4 and particulate acidity have been observed for the first time in California ambient air. The highest level of H_2SO_4 found was 220 neq/m^3 (11 $\mu g/m^3$) for a four-hour period. This compares to California's 24-hour standard of 25 $\mu g/m^3$ for total water soluble sulfate.

2. Particle bound HNO_3 appears to contribute to the observed particulate acidity.

3. The strong dependence of H_2SO_4 levels on wind direction at Lennox suggests that stationary emissions of H_2SO_4 and/or SO_3 were the source of the observed H_2SO_4.

4. Short-term sampling is useful in minimizing losses of H_2SO_4.

5. Glass fiber filters approximate total inorganic nitrate samplers, collecting both atmospheric particulate nitrates and nitric acid.

6. In California's South Coast Air Basin, (as well as in Pittsburg, California as shown in Phase I), nitric acid is the only

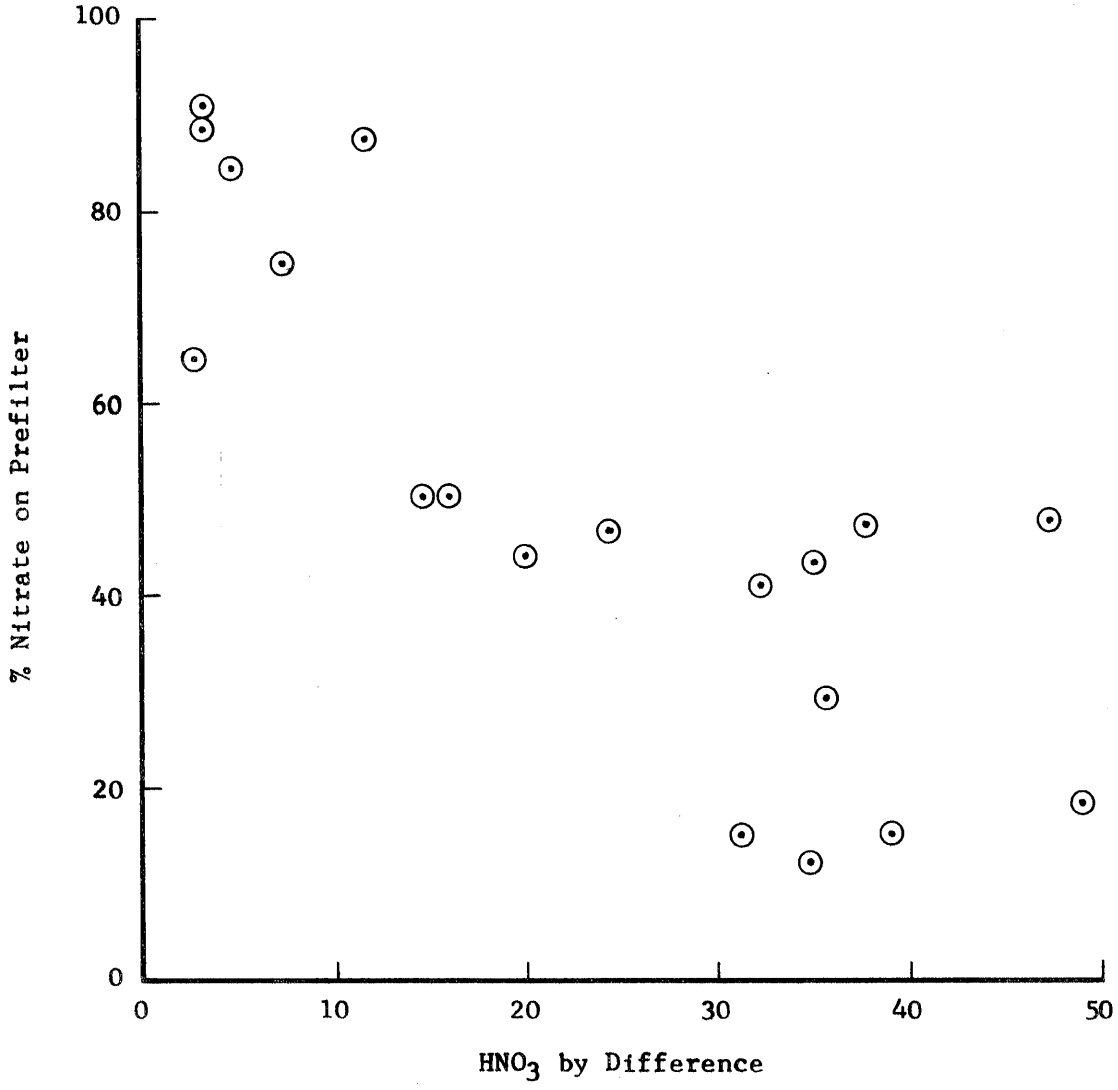


Figure 28 THE PERCENT OF NITRATE ON THE PREFILTER OF THE PARTICULATE NITRATE SAMPLER vs HNO_3 CONCENTRATION

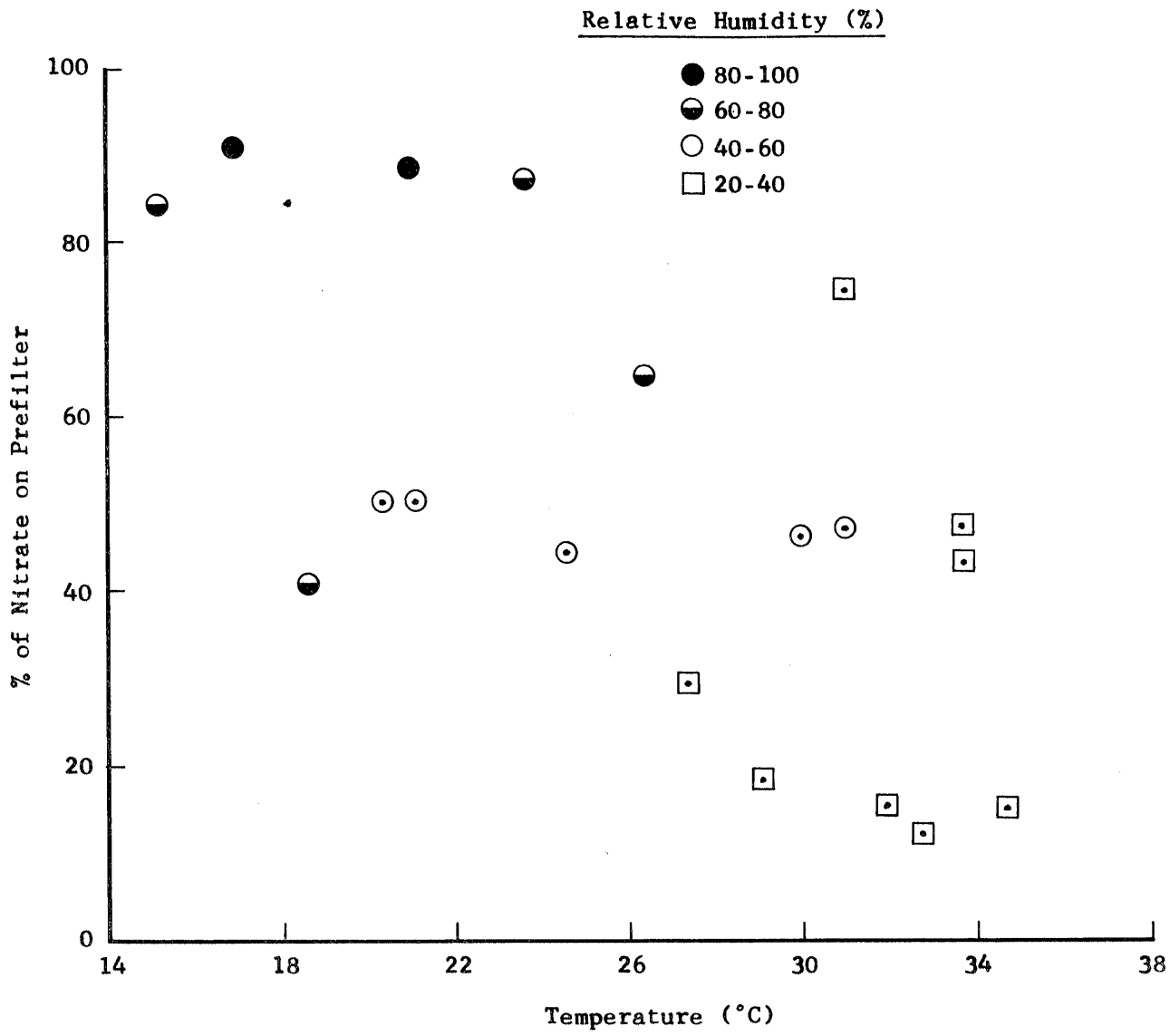


Figure 29 THE PERCENT OF NITRATE ON THE PREFILTER OF THE PARTICULATE NITRATE SAMPLER vs TEMPERATURE.

observable contributor to artifact particulate nitrate formation in atmospheric sampling with glass fiber filters.

7. The heating of filter samplers for particulate nitrate and HNO_3 causes increased error. Even without heating, > 50% losses of particulate nitrate from the Teflon prefilter can occur with corresponding positive errors in HNO_3 measurement.

8. Nitric acid values obtained by difference between total inorganic nitrate and particulate nitrate measurements are too high. Nevertheless, these results are more accurate than those by simple filter collection techniques.

9. Sampling of particulate nitrate with an acid gas denuder, Teflon prefilter and HNO_3 trap provides improved sampling accuracy compared to collection with Teflon filters.

VI. REFERENCES

1. B. R. Appel, Y. Tokiwa, S. M. Wall, M. Haik, E. L. Kothny and J. J. Wesolowski. Determination of Sulfuric Acid, Total Particle-Phase Acidity and Nitric Acid in Ambient Air. Final Report to the Air Resources Board for Contract No. A6-209-30 (1979).

2. T. Okita, S. Morimoto, S. Izawa, and W. Konno. The Measurement of Gaseous and Particulate Nitrates in the Atmosphere. Atmos. Environ. 10 1085-1089 (1976).

3. C. W. Spicer. Measurement of Gaseous HNO_3 by Electrochemistry and Chemiluminescence in "Current Methods to Measure Atmospheric Nitric Acid and Nitrate Artifacts". R. K. Stevens, Editor, EPA Report 600/2-79-051 (1979).

4. A Lazrus. Nitric Acid Measurement in Western USA in "Current Methods to Measure Atmospheric Nitric Acid and Nitrate Artifacts", R. K. Stevens, Editor, EPA Report 600/2-79-051 (1979).

5. B. R. Appel, E. M. Hoffer, M. Haik and J. J. Wesolowski. First Quarterly Progress Report on Sampling and Analytical Problems in Air Pollution Monitoring. EPA Grant No. R806734-01-0 (December 1979).

6. J. Forrest, R. L. Tanner, D. Spandau, T. D'Ottavio and L. Newman. Determination of Atmospheric HNO_3 with NaCl-impregnated Filters at High Volume Flow Rates in "Current Methods to Measure Atmospheric Nitric Acid and Nitrate Artifacts", R. K. Stevens, Editor, EPA Report 600/2-79-051 (1979).

7. A. W. Stelson, S. K. Friedlander and J. H. Seinfeld. A Note on the Equilibrium Relationship Between Ammonia and Nitric Acid and Particulate Ammonium Nitrate. Atmos. Environ. 13 369-371 (1979).

8. A. B. Harker, L. W. Richards and W. E. Clark. The Effects of Atmospheric SO_2 Photochemistry upon Observed Nitrate Concentrations in Aerosols. Atmos. Environ. 11 87-91 (1977).

9. W. R. Pierson, W. W. Brachaczek, T. J. Korniski, T. J. Truex and J. W. Butler, Artifact Formation of Sulfate, Nitrate and Hydrogen Ion on Backup Filters: Allegheny Mountains Experiment. J. Air Poll. Cont. Assoc. 30 30-34 (1980).

10. Calculated from standard free energies of formation given in Lange's Handbook of Chemistry, 12th Ed., McGraw Hill (1979).

11. B. R. Appel, J. J. Wesolowski, E. Hoffer, S. Twiss, S. Wall, S. Chang and T. Novakov. An Intermethod Comparison of X-ray Photoelectron Spectroscopic (ESCA) Analysis of Atmospheric Particulate Matter. Int. J. Environ. Analyt. Chem. 4 169-181 (1976).

12. J. R. Smith. Estimating Overall Sample Train Efficiency. J. Air Poll. Cont. Assoc. 29 969-970 (1979).

13. J. Forrest, R. L. Tanner, D. Spandau, T. D'Ottavio and L. Newman. Determination of Total Inorganic Nitrate Utilizing Collection of Nitric Acid on NaCl-impregnated Filters. Atmos. Environ. 14 137-144 (1980).

14. T. M. Florence and Y. J. Farrar. Spectrophotometric Determination of Chloride in Parts-per-billion level by the Mercury (II) Thiocyanate Method. Anal. Chim. Acta 54 373 (1971).

15. K. Kaneda, T. Yanaka, R. Sugai. Determination of Gaseous and Particulate Chloride and Fluoride in the Atmosphere. Atmos. Environ. 8 927-936 (1974).

16. R. W. Shaw, T. G. Dzubay, R. K. Stevens. The Denuder Difference Experiment in "Current Methods to Measure Atmospheric Nitric Acid and Nitrate Artifacts", R. K. Stevens, Editor, EPA Report 600/2-79-051 (1979).

17. J. L. Durham. Private communication (1980).

18. D. W. Joseph and C. W. Spicer. Chemiluminescence Method for Atmospheric Monitoring of Nitric Acid and Nitrogen Oxides. Anal Chem. 50 1400-1403 (1978).

19. C. W. Spicer, Private communication (1979).

20. C. Brosset. Possible Changes in Aerosol Composition Due to Departure from Equilibrium Conditions during Sampling. Swedish Water and Air Pollution Research Institute Report B454 (1978).

21. C. Brosset. The Acid-base Balance in Lake Water. Swedish Water and Air Pollution Research Institute Report B540 (1980).

22. K. W. Crawford and J. C. Trijonis. Preliminary Report: Development of a Particulate Implementation Plan for the Los Angeles Region - Report No. 2. Emission Inventories and Projection. EPA Contract 68-02-1384.

23. B. R. Appel, S. M. Wall, M. Haik, E. L. Kothny and Y. Tokiwa. Evaluation of Techniques for Sulfuric Acid and Particulate Strong Acidity Measurements in Ambient Air. Atmos. Environ. 14 559-563 (1980).

24. R. L. Tanner, R. Cederwall, R. Garber, D. Leahy, W. Marlow, R. Meyers, M. Phillips and L. Newman. Separation and Analysis of Aerosol Sulfate Species at Ambient Concentration. Atmos. Environ. 11 955-966 (1977).

25. C. Brosset and M. Ferm. Man-made Airborne Acidity and its Determination. Atmos. Environ. 12 909-916 (1978).

26. E. M. Hoffer, E. L. Kothny and B. R. Appel. Simple Method for Microgram Amounts of Sulfate in Atmospheric Particulates. Atmos. Environ. 13 303-306 (1979).

27. Technicon Industrial Systems. Nitrate and Nitrite in Water and Wastewater Method No. 100-70W. Technicon Instruments Corp., Tarrytown, NY (1973).

28. L. W. Richards, L. W. Johnson, L. S. Shepard. Sulfate Aerosol Study. Final Report to the Coordinating Research Council, Contract No. CAPA- 13-76 (1978).

29. W. John and G. Reischl. Measurement of the Filtration Efficiencies of Selected Filter Types. Atmos. Environ. 12 2015-2019 (1978).

30. B. R. Appel, S. M. Wall, Y. Tokiwa and M. Haik. Interference Effects in Sampling Particulate Nitrate in Ambient Air. Atmos. Environ. 13 319-325 (1979).

31. B. R. Appel, S. M. Wall, Y. Tokiwa and M. Haik. Simultaneous Nitric Acid, Particulate Nitrate and Acidity Measurements in Ambient Air. Atmos. Environ. 14 549-554 (1980).

32. D. F. Miller, C. W. Spicer. Measurement of Nitric Acid in Smog. J. Air Poll. Cont. Assoc. 25 940-942 (1975).

33. B. R. Appel, E. L. Kothny, E. M. Hoffer, G. M. Hidy, J. J. Wesolowski. Sulfate and Nitrate Data from the California Aerosol Characterization Experiment (ACHEX). Environ. Sci. and Technol. 12 418-425 (1978).

34. S. Kadowaki. Size Distribution and Chemical Composition of Atmospheric Particulate Nitrate in the Nagoya Area. Atmos. Environ. 11 671-675 (1977).

35. B. R. Appel, Y. Tokiwa, S. M. Wall, E. M. Hoffer, M. Haik and J. J. Wesolowski. Effect of Environmental Variables and Sampling Media on the Collection of Atmospheric Sulfate and Nitrate. Final Report to the California Air Resources Board for Contract 5-1032 (1978). Available as NTIS Report No. PB286480/AS and PB286481/AS.

36. Kirk-Othmer. Encyclopedia of Chemical Technology. 2nd Ed. p. 321, Vol. 2. John Wiley & Sons, Inc. (1963).

37. P. G. Gormley and M. Kennedy, Proc. R. Ir. Acad. 52 163 (1949).